Gregor Skačej
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# Solved Problems in Thermodynamics and Statistical Physics

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*To Mira and Katja*

# Preface

Mastering a topic in physics generally includes solving a suitable set of problems, either in tutorials and homework assignments or while preparing for an examination. Thermodynamics and statistical physics are no exception, although their conceptual framework is seemingly simple, at least at the level of equilibrium phenomena, and they are usually technically undemanding compared to, e.g., theory of elasticity or electromagnetism. Most standard textbooks on thermodynamics and statistical physics do contain some problems that the readers can use to consolidate their knowledge, but the dedicated solved-problems volumes address the development of these specific skills in a more focused, hands-on, and comprehensive fashion. This book belongs to the latter category.

The material included is or has been used in the undergraduate course on statistical thermodynamics for students of physics at the University of Ljubljana. The topics discussed cover the standard syllabus of most such courses from the equation of state to the kinetic theory of gases, and elementary knowledge of classical and quantum physics is sufficient to tackle most problems. With the selection of problems, we wish to emphasize that the theoretical apparatus of thermodynamics and statistical physics is quite universal and that it does not apply solely to *pVT* systems best known from the typical general-physics course for freshmen. This is why we often discuss electric, magnetic, and other non-*pVT* systems, equations of state, etc., so as to offer readers the opportunity to recognize the universality by themselves. At the same time, we put emphasis on examples from soft condensed matter physics, touching upon the many instances where excluded-volume interactions lead to interesting effects. (Here we must refer the interested reader to the excellent *Entropy Beyond the Second Law* by Attard.) In several cases, we resort to seemingly artificial problems, such as when discussing the two-dimensional Fermi gas, because there exists an exact closed-form solution, which is well worth deriving and examining. Some of the problems are actually case studies dealing with selected special topics from different fields of physics. These include the isothermal–isobaric ensemble, Tonks gas, Debye–Hückel theory of plasma, Onsager theory of the nematic–isotropic transition, rubber elasticity, Flory mean-field theory of polymers, transfer-matrix formalism in spin and polymer chains, renormalization group, lattice gas model, etc. A few systems are considered repeatedly but from diverse perspectives: For example, the one-dimensional Ising chain is analyzed using as many as four different approaches, and thermionic emission is studied both within thermodynamics and statistical mechanics.

The book may be of interest primarily to undergraduate students of physics as well as to their instructors, but it may also be helpful as a reference for a course of chemical or engineering thermodynamics. Some of the 234 problems examined are discussed in tutorials and others were developed for the open-notes/open-books style examinations at the University of Ljubljana. Many were originally proposed in the Slovenian-language textbook *Toplota* by Kuščer and Žumer, albeit without solutions, and some are adapted from or inspired by other textbooks. Quite a few were conceived by ourselves. The material contained in this book is intended to be used in tutorials and for self-study, and the book itself is a companion text rather than a self-contained, standalone volume as we did not include any introductory material to review the main concepts in a given topic. When organizing the material into chapters, we arranged the problems according to the main theme; in some cases, this cannot be done unambiguously and hence some arbitrariness in the division.

Our book is hardly the only of its kind; some other references of various styles, coverages, and levels of difficulty are listed at the end where we also mention a few textbooks of interest. The book edited by Lim is a collection of problems from entrance examinations at the universities in the US, which are generally designed to test conceptual knowledge. Abbott–Van Ness' volume of Schaum's Outline is a nice, engineering-oriented thermodynamics-only collection of solved problems. Kubo's classics combine an overview of the main concepts in each topic with problems that span many levels of difficulty. Although not a collection of solved problems, Rumer–Ryvkin's textbook contains many illuminating case studies or worked examples. Equally interesting as these established references are the more recent ones such as the book by Cini, Fucito, and Sbragaglia. In our experience, no single resource suffices by itself, and we strongly suggest consulting both those singled out in the list of references as well as any related titles that we do not mention here.

The style of *Solved Problems in Thermodynamics and Statistical Physics* is intentionally concise and the language is terse. In each solution, we describe all of the main steps but the intermediate ones are left to the readers as an invitation; we are convinced that by working them out, they will better understand the material. Nonetheless, we include an interpretation of the physical phenomenon at hand and references to related topics and problems in the book as appropriate. Most problems ask for a numerical answer; still the emphasis is on concepts. Some figures are included but, in many problems, the readers are expected to sketch one by themselves. Often it is advantageous to consider a suitable simplification of the exact result or a limiting case, which usually provides a physical insight. In some problems, we complement the analytical approximation with the exact numerical result so as to demonstrate how they compare to each other.

The text of problems is typeset in *italic* whereas the solutions are in upright font. The symbols used are generally consistent with most modern textbooks on thermodynamics and statistical physics; unless stated otherwise, "specific" refers to the quantity in question per unit mass. As usual, the heat is positive if it is received by the system and negative if it is emitted, and analogously for work. We use caligraphic fonts $\mathcal{C}$ to indicate reduced (i.e., dimensionless) quantities, the only exception being $\mathcal{F}$ which is used for the magnitude of the force. Vectors and tensors are in upright boldface font $\mathbf{b}$ and in sans-serif font $\mathsf{S}$, respectively; except in one or two instances, primed quantities such as $U'$ denote the initial state and unprimed ones refer to the final state. Some textbooks use a special symbol such as $đ$ to indicate improper differentials; here we assume that readers know that heat and work are not functions of state and that this need not be emphasized every time we write the first and the second law. For conciseness, mathematical material is typeset using the convention where implied multiplication has precedence over division so that $ab/cd$ stands for $(ab)/(cd)$. We use the *Système International* (SI) units. For conciseness, the index does not include the very frequent entries such as energy and heat capacity at constant volume.

This book is largely a translation of two volumes that we wrote in Slovenian. These volumes were reprinted several times before we started working on the translation and we trust that we managed to remove the majority of errors; at this point, we thank all students and colleagues who drew our attention to errors and inconsistencies and helped us to fix them. It is possible that some of them remain and we will appreciate the readers telling us about anything that should be corrected or amended.

We appreciate the unfaltering support of the Faculty of Mathematics and Physics, University of Ljubljana, and we thank our families for their encouragement and understanding. We hope that the readers will like the *Solved Problems* as much as we do—now that they are solved.

Ljubljana, Slovenia
Gregor Skačej
Primož Ziherl

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Part I Thermodynamics

Part II Statistical Physics

# Part I
# Thermodynamics

# Chapter 1
# Equation of State

**Problem 1.1.**
*Rewrite the van der Waals equation of state*

$$\left(p+\frac{a}{V_M^2}\right)(V_M-b)=RT$$

*in terms of reduced variables! Calculate the critical values of pressure* $p_c$*, kilomolar volume* $V_{Mc}$*, and temperature* $T_c$*!*

At the critical point, one has $(\partial p/\partial V_M)_T=0$ and $\left(\partial^2 p/\partial V_M^2\right)_T=0$. By calculating the derivative of the van der Waals equation with respect to $V_M$, we find that the first condition reads $p_c-a/V_{Mc}^2+2ab/V_{Mc}^3=0$. The second one reduces to $2a/V_{Mc}^3-6ab/V_{Mc}^4=0$, which can be solved for $V_{Mc}$ to give

$$V_{Mc}=3b\,.$$

By inserting this result into the first derivative of the van der Waals equation, we obtain

$$p_c=\frac{a}{27b^2}\,,$$

and the equation of state itself then gives

$$T_c=\frac{8a}{27Rb}\,.$$

Now we introduce the reduced variables $\mathcal{P}=p/p_c$, $\mathcal{V}=V_M/V_{Mc}$, and $\mathcal{T}=T/T_c$ so as to recast the van der Waals equation of state as

$$\left(\mathcal{P}+\frac{3}{\mathcal{V}^2}\right)(3\mathcal{V}-1)=8\mathcal{T}\,.$$

G. Skačej and P. Ziherl, *Solved Problems in Thermodynamics and Statistical Physics*, https://doi.org/10.1007/978-3-030-27661-4_1

A few characteristic isotherms including a subcritical one featuring metastable states and liquid–gas coexistence obtained using the Maxwell rule are shown in Fig. 1.1.

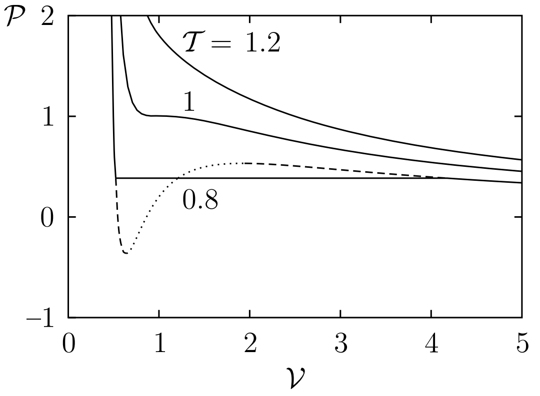

**Fig. 1.1** Van der Waals fluid isotherms at $\mathcal{T} = 0.8$, 1, and 1.2: The dashed line depicts metastable states (superheated liquid and supercooled gas) whereas the dotted line shows unphysical states with negative compressibility. The subcritical isotherm ($\mathcal{T} = 0.8$) is cut into three sections according to the Maxwell rule (see Problem 5.7): The steepest section corresponds to liquid state, the horizontal to liquid–gas coexistence, and the remaining section to gas

### Problem 1.2.

*Find the lowest possible negative pressure in the van der Waals fluid!*

By examining the isotherms we conclude that $\mathcal{P}_{\rm min}$ is observed at $\mathcal{T} = 0$. Since the van der Waals equation of state only allows states with $\mathcal{V} \geq 1/3$, we have $\mathcal{P}_{\rm min} = -27$.

### Problem 1.3.

*Find the maximum superheating temperature of the van der Waals liquid at low pressure!*

Upon isobaric heating, metastable liquid states can be observed before reaching the van der Waals isotherm that exhibits a minimum at the specified pressure. Consequently, we search for the isotherm that has a minimum at zero pressure. We have $\mathcal{P} = 8\mathcal{T}/(3\mathcal{V} - 1) - 3/\mathcal{V}^2 = 0$ and $(\partial\mathcal{P}/\partial\mathcal{V})_\mathcal{T} = -24\mathcal{T}/(3\mathcal{V} - 1)^2 + 6/\mathcal{V}^3 = 0$. These two conditions give $\mathcal{V}^* = 2/3$ and thus

$$\mathcal{T}^* = \frac{27}{32} \approx 0.844\,.$$

### Problem 1.4.

*What is the lowest temperature such that the van der Waals isotherm does not have an inflection point?*

The inflection point is defined by $(\partial^2\mathcal{P}/\partial\mathcal{V}^2)_\mathcal{T} = 144\mathcal{T}/(3\mathcal{V}-1)^3 - 18/\mathcal{V}^4 = 0$, i.e., by $8\mathcal{T}\mathcal{V}^4 - (3\mathcal{V}-1)^3 = 0$. This equation has no roots for

$$\mathcal{T} > \mathcal{T}_{\max} = \max\left(\frac{(3\mathcal{V}-1)^3}{8\mathcal{V}^4}\right).$$

The function $f(\mathcal{V}) = (3\mathcal{V}-1)^3/8\mathcal{V}^4$ is positive for all $\mathcal{V} > 1/3$, has a triple root at $\mathcal{V} = 1/3$, and decreases as $27/8\mathcal{V}$ at large $\mathcal{V}$ (Fig. 1.2). The maximum of $f(\mathcal{V})$ is reached at $\mathcal{V} = 4/3$, which corresponds to

$$\mathcal{T}_{\max} = \frac{2187}{2048} \approx 1.068\,.$$

Above $\mathcal{T}_{\max}$, the isotherms are convex like in the ideal gas.

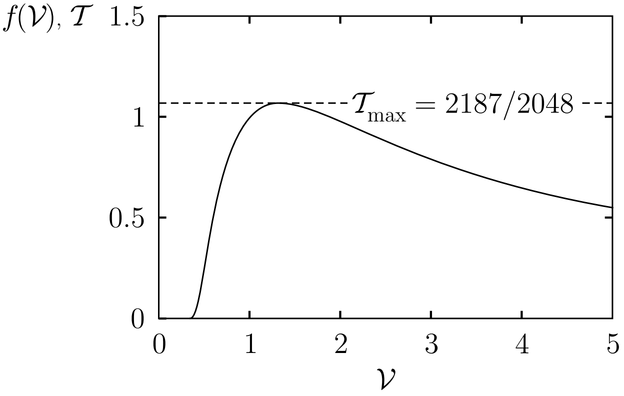

**Fig. 1.2** Inflection points of the van der Waals isotherms: For $\mathcal{T} < \mathcal{T}_{\max} = 2187/2048$, there are two such points whereas above $\mathcal{T}_{\max}$ there are none

**Problem 1.5.**
*Find the isothermal compressibility and the volumetric thermal expansion coefficient of the van der Waals gas!*

The isothermal compressibility is

$$\chi_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = -\frac{1}{p_c\mathcal{V}}\left(\frac{\partial\mathcal{V}}{\partial\mathcal{P}}\right)_\mathcal{T} = \frac{1}{p_c}\frac{(3\mathcal{V}-1)^2\mathcal{V}^2}{6(4\mathcal{T}\mathcal{V}^3 - 9\mathcal{V}^2 + 6\mathcal{V} - 1)}$$

and the volumetric thermal expansion coefficient

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{T_c\mathcal{V}}\left(\frac{\partial\mathcal{V}}{\partial\mathcal{T}}\right)_\mathcal{P} = \frac{1}{T_c}\frac{4(3\mathcal{V}-1)\mathcal{V}^2}{3(4\mathcal{T}\mathcal{V}^3 - 9\mathcal{V}^2 + 6\mathcal{V} - 1)}\,.$$

Both quantities diverge at the critical point where $\mathcal{T} = 1$ and $\mathcal{V} = 1$.

### Problem 1.6.

*Rewrite the critical van der Waals isotherm in a simplified form valid close to the critical point!*

We introduce $\mathcal{P} = 1 + \mathcal{X}$ and $\mathcal{V} = 1 + \mathcal{Y}$, where $\mathcal{X}$ and $\mathcal{Y} \ll 1$, and we set $\mathcal{T} = 1$ so that the van der Waals equation of state reads $1 + \mathcal{X} + 3/(1+\mathcal{Y})^2 = 8/(2+3\mathcal{Y})$. By substituting $(1+u)^{-1}$ by $1 - u + u^2 - u^3 + \ldots$ and $(1+u)^{-2}$ by $1 - 2u + 3u^2 - 4u^3 + \ldots$, we obtain $\mathcal{X} = -3\mathcal{Y}^3/2$ or

$$\mathcal{P} - 1 = -\frac{3}{2}\,(\mathcal{V} - 1)^3\,.$$

Close to the critical point, the simplified isotherm agrees well with the exact one as suggested by Fig. 1.3.

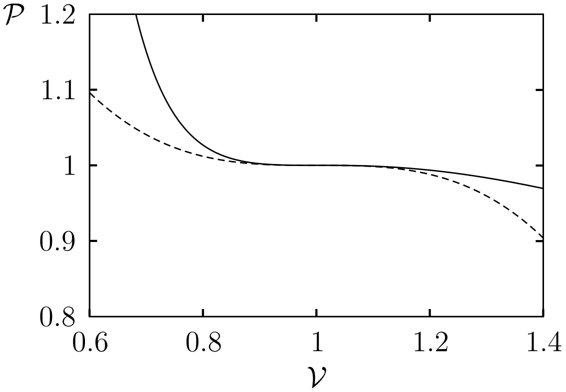

**Fig. 1.3** Critical van der Waals isotherm: Approximate (dashed line) versus exact isotherm (solid line)

### Problem 1.7.

*Rewrite the first Dieterici equation of state*

$$p\,(V_M - b) = RT \exp\left(-\frac{a}{RTV_M}\right)$$

*using reduced variables! Find the critical pressure, volume, and temperature!*

Like in Problem 1.1, we arrive at $V_{Mc} = 2b$, $p_c = \exp(-2)a/4b^2$, $T_c = a/4Rb$ and obtain

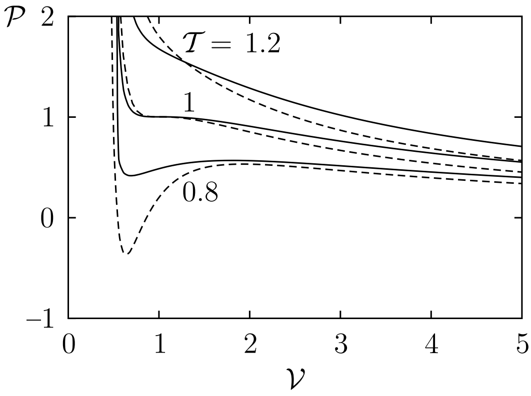

**Fig. 1.4** Dieterici isotherms (solid lines; plotted for $\mathcal{T} = 0.8$, 1, and 1.2) are qualitatively similar to the van der Waals isotherms (dashed lines)

$$\mathcal{P}(2\mathcal{V} - 1) = \mathcal{T} \exp\left(-\frac{2}{\mathcal{T}\mathcal{V}} + 2\right).$$

A few characteristic isotherms are shown in Fig. 1.4.

### Problem 1.8.

*Calculate the isothermal compressibility of fog!*

Fog consists of saturated moist air and tiny yet visible water droplets, which ensure that the air is saturated. We neglect the compressibility of droplets and write $p = p_a + p_s$ in agreement with Dalton's law.

Here, $p_a$ and $p_s$ denote the partial pressures of dry air and water vapor, respectively, and $p$ is the total pressure. Air is treated as an ideal gas so that $p_a = p - p_s = m_a RT/M_a V$ (where $m_a$ and $M_a$ stand for the mass of dry air and kilomolar mass, respectively, and $V$ stands for the total volume), and from here it follows that $V = m_a RT/M_a(p - p_s)$. Since $p_s$ only depends on temperature, we have

$$\chi_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \frac{m_a RT}{V M_a[p - p_s(T)]^2} = \frac{1}{p - p_s(T)}.$$

The temperature dependence of the saturated water vapor pressure is given by the Clausius–Clapeyron equation: $\mathrm{d}p_s/\mathrm{d}T = p_s M_w q_v(T)/RT^2$, where $q_v(T) = q_v(T_0) + \Delta c_p(T - T_0)$ is the heat of vaporization and $\Delta c_p = c_p^g - c_p^l$ is the difference of heat capacities; here the superscripts refer to gas and liquid, respectively, and $M_w$ is the kilomolar mass of water. We also assumed that the density of vapor is much smaller than that of liquid water. Finally, we obtain

$$p_s(T) = p_s(T_0)\exp\left(-\frac{M}{R}\left\{\left[q_v(T_0) - \Delta c_p T_0\right]\left(\frac{1}{T} - \frac{1}{T_0}\right) - \Delta c_p \ln\frac{T}{T_0}\right\}\right),$$

where $p_s(T_0)$ is the reference saturated vapor pressure. This expression can be simplified to $p_s(T) = p_s(T_0)\exp\bigl(-Mq_v\,(1/T - 1/T_0)\,/R\bigr)$ if the temperature range considered is narrow enough and the temperature dependence of the heat of vaporization $q_v$ is neglected.

### Problem 1.9.

*Find the isothermal Young modulus and the thermal expansion coefficient of a rubber band! Its equation of state relates the applied force $\mathcal{F}$ to band length $\ell$ and temperature $T$, and is given by*

$$\frac{\mathcal{F}}{A} = aT\left\{\frac{\ell}{\ell_0} - [1 + \sigma(T - T_0)]\left(\frac{\ell_0}{\ell}\right)^2\right\},$$

*where $\ell_0$ denotes the band length at zero load and temperature $T_0$, and $A$ its cross section, whereas $a$ and $\sigma$ are constants.*

The Young modulus is equal to

$$E_T = \frac{\ell}{A}\left(\frac{\partial\mathcal{F}}{\partial\ell}\right)_T = aT\left\{\frac{\ell}{\ell_0} + 2\,[1 + \sigma(T - T_0)]\left(\frac{\ell_0}{\ell}\right)^2\right\}$$

and the thermal expansion coefficient reads

$$\alpha = \frac{1}{\ell}\left(\frac{\partial\ell}{\partial T}\right)_{\mathcal{F}} = \frac{1}{T}\,\frac{-\ell/\ell_0 + [1 + \sigma(2T - T_0)]\,(\ell_0/\ell)^2}{\ell/\ell_0 + 2\,[1 + \sigma(T - T_0)]\,(\ell_0/\ell)^2}\,.$$

For $\ell = \ell_0$ and $T = T_0$, one has $\alpha = \sigma/3$.

### Problem 1.10.

*Estimate the electric dipole moment of a water molecule! The relative permittivity of water vapor at* 100 °C *and* 1 bar *is equal to* 1.0078, *whereas the electric polarization of vapor is given by*

$$P = np_e\left(\coth\frac{p_eE}{k_BT} - \frac{k_BT}{p_eE}\right),$$

*where $n$ is the number density of water molecules, $p_e$ is the dipole moment, $E$ is the electric field strength, and $k_B$ is the Boltzmann constant!*

We focus on the behavior of water vapor in the linear regime, where $P = \epsilon_0(\epsilon - 1)E$, i.e., in a weak electric field. Then, we have $p_eE/k_BT \ll 1$ and hence $\coth\,(p_eE/k_BT) \approx k_BT/p_eE + p_eE/3k_BT$ so that

$$P(T \gg p_eE/k_B) \approx \frac{np_e^2E}{3k_BT}\,.$$

In this regime, the susceptibility of water vapor is described by the Curie law $\chi = \epsilon - 1 = \epsilon_0^{-1}\,(\partial P/\partial E)_{E=0} = np_e^2/3\epsilon_0k_BT$ as illustrated in Figure 1.5.

The molecular density can be estimated from the equation of state of ideal gas, $n = p/k_BT$, yielding

$$p_e = \sqrt{\frac{3\chi\epsilon_0}{p}}k_BT = 7.4 \times 10^{-30}\ \mathrm{Asm}\,.$$

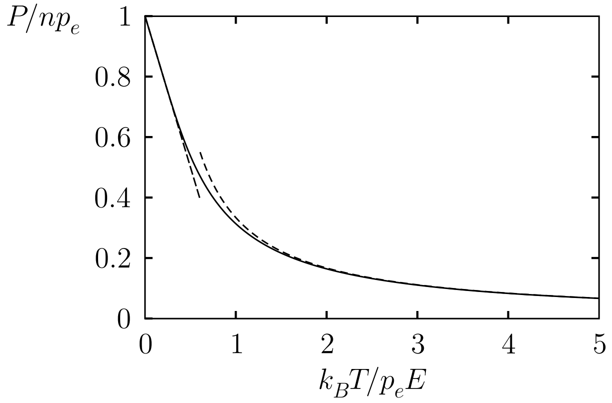

**Fig. 1.5** Temperature dependence of electric polarization in a rarefied gas of molecules carrying permanent electric dipoles (solid line): At low temperatures the polarization is a linear function of $T$, whereas at high temperatures it falls off as $1/T$ (Curie law; dashed line)

Note also that at low temperature, one obtains

$$P(T \ll p_eE/k_B) \approx np_e\left(1 - \frac{k_BT}{p_eE}\right).$$

**Problem 1.11.**
*Explore the temperature dependence of the magnetic susceptibility in a spin-*$1/2$ *ferromagnet just below the transition temperature! The average magnitude of the projection of the magnetic dipole onto the external magnetic field is determined by*

$$\frac{\overline{p_z}}{p_B} = \tanh\left(\frac{p_B}{k_BT}\left(\mu_0H + \frac{zJ}{4p_B}\frac{\overline{p_z}}{p_B}\right)\right),$$

*where* $p_B = e_0\hbar/2m_e$ *denotes the Bohr magneton,* $z$ *is the number of nearest neighbors in the crystal lattice, and* $J$ *is the exchange integral. The ferromagnetic–paramagnetic transition temperature is* $zJ/4k_B$.

The equation of state is first rewritten in terms of reduced quantities: $\mathcal{M} = \overline{p_z}/p_B$ denotes the ratio of magnetization $M$ at a given temperature and the saturated magnetization at $T = 0$, $\mathcal{H} = 4p_B\mu_0H/zJ$ is the reduced magnetic field strength, and $\mathcal{T} = T/T_c$ (where $T_c = zJ/4k_B$) is the reduced temperature. In these units, the ferromagnetic–paramagnetic transition is at $\mathcal{T} = 1$ and the above equation of state reads

$$\mathcal{M} = \tanh \frac{\mathcal{H} + \mathcal{M}}{\mathcal{T}} .$$

We would like to find the magnetic susceptibility $\chi = (\partial M/\partial H)_T$ in a weak external field and just below the transition temperature (i.e., at $\mathcal{H} \to 0$ and $\mathcal{T} \to 1$) where magnetization is small. By expanding $\tanh u \approx u - u^3/3 + \ldots$, we have

$$\mathcal{M} \approx \frac{\mathcal{H} + \mathcal{M}}{\mathcal{T}} - \frac{(\mathcal{H} + \mathcal{M})^3}{3\mathcal{T}^3} .$$

Thus, in absence of external field the equilibrium magnetization equals $\mathcal{M}(\mathcal{T}, \mathcal{H} = 0) = \sqrt{3\mathcal{T}^2(1 - \mathcal{T})}$. To obtain the magnetic susceptibility, we differentiate the above equation. In the limit of $\mathcal{H} = 0$, we have

$$\mathrm{d}\mathcal{M} \approx \frac{\mathrm{d}\mathcal{H}}{\mathcal{T}} + \frac{\mathrm{d}\mathcal{M}}{\mathcal{T}} - \frac{\mathcal{M}^2}{\mathcal{T}^3}\,\mathrm{d}\mathcal{H} - \frac{\mathcal{M}^2}{\mathcal{T}^3}\,\mathrm{d}\mathcal{M} .$$

In this case, $\chi \propto (\partial \mathcal{M}/\partial \mathcal{H})_{\mathcal{T}} = \left(\mathcal{T}^2 - \mathcal{M}^2\right) / \left(\mathcal{T}^3 - \mathcal{T}^2 + \mathcal{M}^2\right)$. Upon inserting $\mathcal{M}^2 = 3\mathcal{T}^2\,(1 - \mathcal{T})$, we find that $\chi \propto (3\mathcal{T}/2 - 1) / (1 - \mathcal{T})$ so that close to the transition $\chi \approx (1/2)\,(1 - \mathcal{T})^{-1}$. An even more instructive form of this result is obtained by substituting $\mathcal{T}$ by $T/T_c$:

$$\chi \propto (T_c - T)^{-1}.$$

# Chapter 2
# The First Law

**Problem 2.1.**
*A thermally insulated vessel fitted with a large valve contains air at* $50\,^\circ\mathrm{C}$ *and* $0.5$ bar. *The valve is opened so that additional air from the surrounding atmosphere at* $0\,^\circ\mathrm{C}$ and $1$ bar *enters the vessel. What is the temperature of air in the vessel after it comes to rest but before it exchanges any heat with the walls?*

We consider two subsystems: The air that enters the vessel from outside and the air present in the vessel before the valve is opened (Fig. 2.1). For the first subsystem in the initial state we write $p_1 V_1' = m_1 R T_1'/M$;

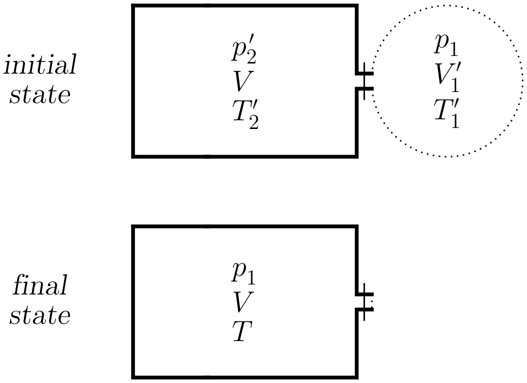

**Fig. 2.1** Ambient air entering a thermally insulated vessel, with the two subsystems physically separated from each other in the initial state

here $p_1$ and $T_1'$ are the ambient pressure and temperature, respectively, whereas $V_1'$ is the (unknown) initial volume of air to be pushed into the vessel after the valve is opened. For the second subsystem, we have $p_2' V = m_2 R T_2'/M$ in the initial state,

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where $p_2'$ and $T_2'$ are the initial pressure and temperature and $V$ is the vessel volume. In the final state, the equation of state reads $p_1V = (m_1 + m_2)RT/M$; here $T$ denotes the final temperature. The atmosphere expends work on the air pushed into the vessel; the work supplied to this mass of air is $W = p_1V_1'$. Since there is no heat exchange between the system and the environment, the first law for the air that ends up in the vessel in the final state reads $p_1V_1' = m_1c_V(T - T_1') + m_2c_V(T - T_2')$, where $T$ is the final temperature. From the three equations of state we extract the work supplied $p_1V_1'$ as well as $m_1$ and $m_2$. From the first law, we finally obtain

$$T = \kappa T_1'\left[1 + \frac{p_2'}{p_1}\left(\kappa\frac{T_1'}{T_2'} - 1\right)\right]^{-1} = 350\ \mathrm{K}.$$

Here we introduced $\kappa = c_p/c_V$ and took into account that in an ideal gas, the difference in specific heat capacities $c_p - c_V = R/M$.

Limiting cases: For an initially evacuated vessel ($p_2' = 0$) we have $T = \kappa T_1'$, whereas for a vessel initially containing air at an ambient temperature and pressure ($p_2' = p_1$ and $T_2' = T_1'$) the temperature remains unchanged as expected, i.e., $T = T_2'$.

**Problem 2.2.**
*A thermally insulated cylinder with a movable light piston contains air at an ambient pressure* 1 bar *and temperature* 20 °C *as well as an ampoule with* 0.5 l *of air at* 3 bar *and* 100 °C; *the initial total volume of the chamber is* 2 l. *The ampoule explodes. What are the final volume and temperature of air in the chamber? No heat is exchanged with the walls and the piston; the walls of the ampoule are very thin and the heat capacity ratio for air is* 7/5.

In the initial state, we have $p'V_1' = m_1RT_1'/M$ for the air in the ampoule and $pV_2' = m_2RT_2'/M$ for the air in the chamber, where $p$ is the pressure in the chamber and in the atmosphere (Fig. 2.2). The final chamber volume and temperature, $V$ and

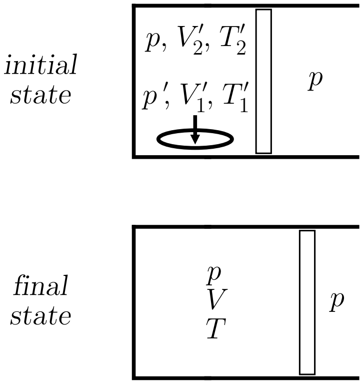

**Fig. 2.2** Air in the chamber expends work against constant atmospheric pressure

$T$, are determined by mechanical equilibrium and the first law. The pressure in the chamber must be equal to the ambient pressure so that $p = (m_1 + m_2)RT/MV$. Since the chamber is insulated, the first law for the air in it reduces to $\Delta U = W$ (where $\Delta U$ denotes the change of internal energy) or

$$(m_1 + m_2)c_V T - m_1 c_V T_1' - m_2 c_V T_2' = -p\left[V - (V_1' + V_2')\right]$$

as the air expends work against constant ambient pressure. This result can be combined with the above equations of state to obtain

$$V = \left(1 + \frac{p'/p - 1}{\kappa}\right) V_1' + V_2' = 2.71\ \mathrm{l},$$

where $R/Mc_V = \kappa - 1$. The final temperature reads

$$T = \left(\frac{p'}{p}\frac{V_1'}{VT_1'} + \frac{V_2'}{VT_2'}\right)^{-1} = 297\ \mathrm{K}.$$

**Problem 2.3.**

*A horizontal cylinder is divided into two evacuated chambers by a movable piston. The first chamber has a large valve which connects it to the ambient atmosphere at* 20 °C *and* 1 bar, *whereas the second one is sealed. The piston is attached to the cylinder wall by a spring; as long as the spring is undeformed, the volume of the first chamber is* 1 l. *The inner diameter of the piston is* 6 cm *and the spring constant* $10^3$ N/m. *The valve is opened so that air can enter the first chamber. What is the temperature of air in the cylinder once it comes to rest if the air exchanges no heat with the cylinder?*

The ambient atmosphere ensures that the process is isobaric at pressure $p$. In the final state, $p = kh/A$, where $k$ and $h$ are the spring constant and displacement, respectively, and $A$ is the cross section of the cylinder. The final volume of the first chamber is then given by $V = \overline{V} + Ah = \overline{V} + pA^2/k$; $\overline{V}$ denotes the initial volume of the chamber (Fig. 2.3). The expansion of air into the cylinder is described by the Gay–Lussac law $V'/T' = V/T$, where $V'$ is the volume of air that enters the cylinder in the initial state before the valve is opened and $T'$ the temperature of the atmosphere. From here one has $V' = \left(\overline{V} + pA^2/k\right) T'/T$. The first law for the air that enters the cylinder reads $mc_V(T - T') = pV' - kh^2/2 = pV' - p^2A^2/2k$, where the right-hand side includes work supplied to the air by the atmosphere and the work expended by the air against the spring. Since $pV' = mRT'/M$, we further have $T - T' = (\kappa - 1)\left(T' - pA^2T/2kV\right)$ and finally we obtain

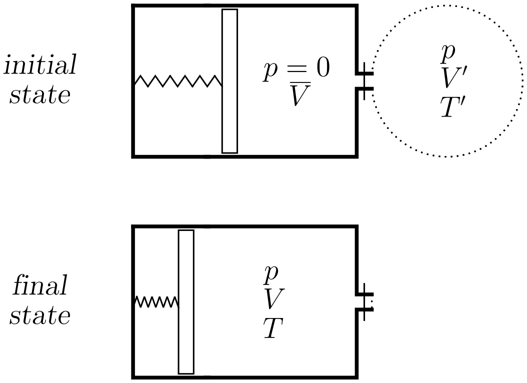

**Fig. 2.3** Ambient atmosphere expends work against the air pushed into the evacuated cylinder, and the air in turn expends work against the spring

$$T = \kappa T' \left(1 + \frac{\kappa - 1}{2} \frac{1}{1 + \overline{V}k/pA^2}\right)^{-1} = 376.6\ \mathrm{K}.$$

Limiting cases: If we set the initial volume of the first chamber $\overline{V}$ to 0 we have $T = 2\kappa T'/(\kappa + 1)$. For a very stiff spring with $k \to \infty$, the final temperature $T = \kappa T'$ coincides with the result of Problem 2.1.

**Problem 2.4.**
*Two one-liter thermally insulated vessels are connected by a valve. The first vessel contains air at* 1 bar *and* 20 °C*, whereas the second one is evacuated. What are the temperatures of air in both vessels immediately after the valve is opened so that the pressures are equalized? No heat is exchanged with the walls of the vessels and the valve. What is the final state if the second vessel initially contains air at* 0.5 bar *and* 100 °C *instead of being empty?*

The system as a whole exchanges neither work nor heat with the environment; hence $\Delta U = \Delta U_1 + \Delta U_2 = m_1 c_V (T_1 - T_1') + m_2 c_V (T_2 - T_1') = 0$, where $m_1$ and $m_2$ denote the final masses of air in the first and the second vessel, respectively, and $T_1$ and $T_2$ are the corresponding temperatures; $T_1'$ is the initial temperature or air in the first vessel. It follows that

$$m_1 T_1 + m_2 T_2 = m_1' T_1' ,$$

where $m_1' = m_1 + m_2$ is the total mass of air. In the final state the vessels are in mechanical equilibrium so that $p_1 = p_2$ and thus $m_1 R T_1 / MV = m_2 R T_2 / MV$, where $V$ is the volume of each vessel. Hence

$$m_1 T_1 = m_2 T_2 ,$$

which yields, together with the above relation obtained from the first law, $2m_1T_1 = 2m_2T_2 = m_1'T_1'$.

The air that remains in the first vessel expends work on the rest of the air but exchanges no heat with it or with the environment. At any stage of the process, the first law for the air in the first vessel reads $m_1c_V\,\mathrm{d}T_1 = -p_1\,\mathrm{d}V_1$. Since the mass of air in the first vessel decreases upon expansion when air is pushed into the second vessel, we have $\mathrm{d}V_1 = -\mathrm{d}m_1/\rho_1$. As $\rho_1 = m_1/V$ this gives $m_1c_V\,\mathrm{d}T_1 = (RT_1/M)\,\mathrm{d}m_1$, and upon inserting $R/M = c_p - c_V$ and $\kappa = c_p/c_V$ we find that $\mathrm{d}T_1/T_1 = (\kappa - 1)\,\mathrm{d}m_1/m_1$. By integrating from the initial to the final state we obtain

$$\frac{m_1}{m_1'} = \left(\frac{T_1}{T_1'}\right)^{1/(\kappa-1)}.$$

An alternative approach leading to the same result is to realize that the air that remains in the first vessel in the final state undergoes a reversible adiabatic process described by $pV^\kappa = const.$; we then use this relation together with the relevant equations of state. —Since we also have $2m_1T_1 = m_1'T_1'$ or $m_1/m_1' = T_1'/2T_1$, we finally find that

$$\frac{T_1'}{2T_1} = \left(\frac{T_1}{T_1'}\right)^{1/(\kappa-1)}$$

or

$$T_1 = T_1'2^{1/\kappa-1} = 240\text{ K}.$$

The masses of air in the two vessels are $m_1 = m_1'T_1'/2T_1 = 0.61\,m_1'$ and $m_2 = m_1' - m_1 = 0.39\,m_1'$, and the final temperature of air in the second vessel reads

$$T_2 = \frac{m_1T_1}{m_2} = 375\text{ K}.$$

This analysis can be generalized to the case where the second vessel is initially not evacuated. Now the first law is rewritten as $\Delta U = \Delta U_1 + \Delta U_2 = (m_1c_VT_1 - m_1'c_VT_1') + (m_2c_VT_2 - m_2'c_VT_2') = 0$ or

$$m_1T_1 + m_2T_2 = m_1'T_1' + m_2'T_2',$$

where $m_1'$ and $m_2'$ are the initial masses of air in the two vessels, whereas $T_1'$ and $T_2'$ are the corresponding temperatures. Mechanical equilibrium still implies that $m_1T_1 = m_2T_2$. Some care is required when considering the first law for a subsystem. It is easiest to write it for the air that remains in the vessel with the higher initial pressure as there will be a net flow of air from higher to lower pressure after the valve is opened (Fig. 2.4). Alternatively, one can also apply the first law to the air that ends up in the lower pressure vessel, but this is somewhat more tricky because this mass of air consists of air initially present in this vessel and of air that enters in from the higher pressure vessel. —In our case, the initial pressure in the first vessel is

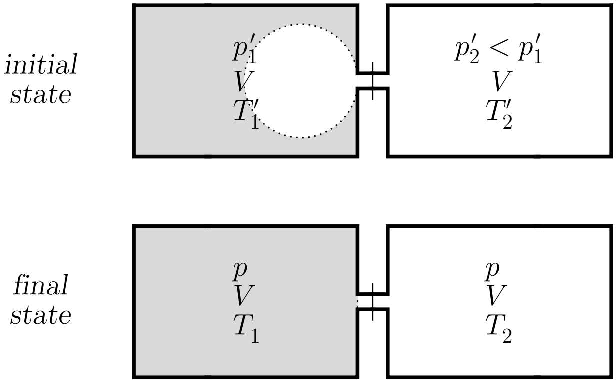

**Fig. 2.4** After the valve is opened, air flows from the first vessel to the second one where the pressure is lower. The air that remains in the first vessel (shaded) expands adiabatically, pushing some air from this vessel into the second one

higher than the pressure in the second one: $p_1' > p_2'$. Following the same reasoning as in the first part of this Problem, we have $m_1/m_1' = \left(T_1/T_1'\right)^{1/(\kappa-1)}$. By writing $m_1' = p_1'VM/RT_1'$ and $m_2' = p_2'VM/RT_2'$, we find that

$$T_1 = T_1' \left(\frac{2}{1 + p_2'/p_1'}\right)^{1/\kappa - 1} = 270\ \mathrm{K}.$$

Since $m_1 = \left(m_1'T_1' + m_2'T_2'\right)/2T_1$ and $m_2 = m_1' + m_2' - m_1$,

$$T_2 = \frac{m_1 T_1}{m_2} = 380\ \mathrm{K}.$$

### Problem 2.5.

*A five-liter tank contains oxygen at an initial pressure of* 10 bar *and a constant temperature of* 20 °C. *Half of the gas is allowed to slowly escape. How much heat is supplied to the gas by the thermostat during this process?*

As the process is slow, we may assume that the oxygen in the tank expands isothermally. The internal energy of the gas present in the tank at any given time thus does not change; therefore heat must be supplied to the gas in the tank by the thermostat to compensate for the work expended on the gas that is being pushed out. The work expended by the oxygen in the tank is

$$W = -\int_0^{m'/2} p\,\mathrm{d}V = -\int_0^{m'/2} \frac{(m' - m)RT}{MV} \frac{\mathrm{d}m}{\rho},$$

where we integrate over the mass of oxygen that escapes from the tank; $m'$ stands for the initial mass of oxygen in the tank whereas $V$ is the tank volume. Since

$\rho = (m' - m)/V$, we have

$$W = -\frac{RT}{M}\int_0^{m'/2} \mathrm{d}m = -\frac{p'V}{2} = -2.5\ \mathrm{kJ}\,.$$

The thermostat supplies 2.5 kJ of heat to the oxygen.

**Problem 2.6.**

*Identical vessels are connected by a thermally insulated valve, which is initially closed. The first vessel is evacuated and in contact with a thermostat, whereas the second vessel contains air at* $20\,^\circ\mathrm{C}$ *and is thermally insulated. The valve is slightly opened such that the first vessel remains in equilibrium with the thermostat at* $20\,^\circ\mathrm{C}$. *Once the pressures in the vessels equalize, the valve is closed. Find the final temperature of air in the second vessel!*

After pressures equalize, we have $m_1T_1 = m_2T_2$; here $m_1$ and $m_2$ are the masses of air in the first and in the second vessel, respectively, $T_1$ is the temperature of the thermostat, and $T_2$ is the final temperature of air in the second vessel. The air in the second vessel receives no heat so that $m_2c_V\,\mathrm{d}T_2 = -p_2\,\mathrm{d}V_2$ and as in Problem 2.4 we obtain $m_2/m_2' = \left(T_2/T_2'\right)^{1/(\kappa-1)}$ with $m_2' = m_1 + m_2$ since initially the first vessel is evacuated. This relation and $m_2 = m_2'T_1/(T_1 + T_2)$, which follows from the condition of mechanical equilibrium, together result in

$$\left(1 + \frac{T_2}{T_1}\right)\left(\frac{T_2}{T_2'}\right)^{1/(\kappa-1)} = 1.$$

This equation can only be solved numerically: $T_1 = T_2'$ and $\kappa = 1.4$ give $T_2 = 0.792\,T_2' = 232$ K. The final pressure is $0.442\,p_2'$, where $p_2'$ stands for the initial pressure in the thermally insulated vessel.

**Problem 2.7.**

*A thermally insulated valve connects two identical vessels. The first one is immersed into a thermostat and contains air at* $20\,^\circ\mathrm{C}$; *the second one is evacuated and thermally insulated. The valve is slightly opened so as to keep the first vessel in equilibrium with the thermostat at all times. Calculate the final air temperature in the insulated vessel after pressures become equal, assuming that no heat is exchanged between the air and the walls of the second vessel!*

The air that is pushed from the first to the second vessel receives work from the air that remains in the first vessel: $W_2 = -W_1 = \int p_1\,\mathrm{d}V_1 = (RT_1/M)\int_0^{m_2}\mathrm{d}m_2 = m_2RT_1/M$, where $T_1$ is temperature of the thermostat and $m_2$ is the final mass of air in the second vessel. The first law gives $m_2c_V(T_2 - T_1) = m_2RT_1/M$ and from here one obtains

$$T_2 = T_1 + \frac{R}{Mc_V} T_1 = \kappa T_1 = 410\ \mathrm{K}.$$

Once the pressures in the two vessels equalize, we can write $m_1 T_1 = (m_1' - m_1) T_2 = m_2 T_2$ or $m_2 = m_1'/(\kappa + 1) = 0.42\, m_1'$ and $m_1 = 0.58\, m_1'$, which yields the final pressure $p_1 = p_2 = [\kappa/(\kappa + 1)]\, p_1'$, where $p_1'$ is the initial pressure in the first vessel.

**Problem 2.8.**
*An evacuated vessel of negligible heat capacity is immersed into boiling water at* $100\,^\circ\mathrm{C}$ *and* 1 bar. *The vessel is fitted with a valve, which is briefly opened so as to equalize the pressure within the vessel with the ambient pressure. Find the fraction of water that evaporates during the process!*

The temperature and the pressure of water pushed into the vessel by the surrounding water remain unchanged. The work expended by the surrounding water is $pV$, where $V$ is the initial volume of water that enters the vessel. This results in an increase of internal energy of this body of water; a part of it evaporates in order to establish the equilibrium between the boiling water and vapor. We thus have $\Delta U = m_v(q_v - RT/M) = pV$ and $V = m_l/\rho_l$, where $m_v$ is the mass of vapor whereas $m_l$ and $\rho_l$ denote the mass and the density of water that enters the vessel, respectively. The mass fraction of the evaporated water is

$$\frac{m_v}{m_l} = \frac{p}{\rho_l(q_v - RT/M)} = 5.1 \times 10^{-5}.$$

The vapor–water volume ratio in the vessel is much larger—approximately $V_v/V_l \approx m_v\rho_l/m_l\rho_v = 0.081$ (here $\rho_v$ is the density of vapor). The mass of water in the vessel is only slightly smaller than $m_l$. Here we used data from the steam tables for water (see Appendix A): At $100\,^\circ\mathrm{C}$ one has $\rho_l^{-1} = 1.043\ \mathrm{dm^3/kg}$ and $\rho_v^{-1} = 1.673\ \mathrm{m^3/kg}$.

**Problem 2.9.**
*A thermally insulated and evacuated one-liter vessel contains an ampoule with* 200 g *of boiling water at* 1 bar. *The ampoule breaks. Find the approximate value of the final temperature of the system provided that the heat capacities of the vessel and the ampoule are negligible!*

After the ampoule breaks, a small amount of water evaporates so as to establish the equilibrium between water and vapor, whereas the rest of water slightly cools down (Fig. 2.5). In the process, the internal energy of the system does not change: $m_v(q_v - RT'/M) - m_l c_V^l\, \Delta T = 0$. Here $m_v$ is the mass of vapor, $m_l$ is the mass of water, and $\Delta T = T' - T > 0$ is the temperature drop; $T'$ and $T$ are the initial and the final temperature, respectively. We neglect the heat capacity of vapor. Therefore

$$\Delta T = \frac{m_v(q_v - RT'/M)}{m_l c_V^l}.$$

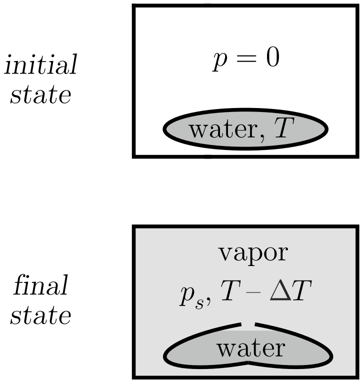

**Fig. 2.5** As the volumes of the vessel and the ampoule containing boiling water are comparable, only a small amount of water evaporates after the ampoule is broken. This, in turn, results in a rather small temperature change

The mass of vapor is obtained from

$$m_v = \frac{p_s(T)V_vM}{RT},$$

where $V_v$ denotes the volume of vapor and $p_s(T)$ is the saturated vapor pressure at temperature $T$. For small temperature changes $V_v$ can be approximated by the difference of volumes of the vessel and the ampoule denoted by $\Delta V$. This can be done because only a small amount of water evaporates and, consequently, in equilibrium the volume of water is only slightly smaller than the volume of the ampoule. Then we find $m_v \approx p_s(T')\,\Delta VM/RT' = 0.464$ g and

$$\Delta T \approx 1.15 \text{ K}.$$

If the ampoule were much smaller than the vessel, a significant part of water would evaporate before the vapor–water equilibrium is established. In this case the above equations have to be solved numerically by taking into account the temperature dependence of the saturated vapor pressure.

**Problem 2.10.**
*A tank containing* 1 kg *of boiling water is placed in an evacuated container immersed in a thermostat at* 100 °C. *The volume of the container is* 1 $\mathrm{m}^3$. *How much heat does the container exchange with the thermostat after the wall of the tank is broken? What is the result if this happens at* 52 °C*? The heat of vaporization is* 2.257 MJ/kg *at* 100 °C *and* 2.377 MJ/kg *at* 52 °C, *and the saturated vapor pressure is* 1.0133 *bar at* 100 °C. *The molar mass of water is* 18 kg/kmol.

We first consider the case of the thermostat at $T' = 100\,^\circ\mathrm{C}$. Evaporation of water from the tank will cease once the saturated vapor pressure $p_s(T')$ is reached; during evaporation at $T'$ the temperature does not change. In equilibrium, the mass of vapor is $m_v' \approx p_s(T')(V_0 - V_1)M/RT' = 0.59$ kg, where $V_0$ and $V_1 \approx 1\ \mathrm{dm}^3$ denote the container and tank volume, respectively. The heat needed for evaporation into vacuum is supplied by the thermostat and reads

$$m_v'\left[q_v(T') - \frac{RT'}{M}\right] \approx 1.22\ \mathrm{MJ}\,,$$

where $q_v(T')$ denotes the heat of vaporization at $T'$.

At the lower temperature of the thermostat $T'' = 52\,^\circ\mathrm{C}$, the final saturated vapor pressure is lower than at $T'$. We calculate it using the Clausius–Clapeyron equation

$$\frac{\mathrm{d}p_s}{\mathrm{d}T} = \frac{q_v(T)}{T\left(\rho_v^{-1} - \rho_l^{-1}\right)} \approx \frac{p_s M \bar{q}_v}{RT^2}\,,$$

where we took into account that the density of vapor $\rho_v = p_s M/RT$ is much smaller than that of water $\rho_l$. Note also that the heat of vaporization depends on temperature; we inserted its mean value $\bar{q}_v = [q_v(T') + q_v(T'')]/2$. After integration one obtains

$$p_s(T'') = p_s(T')\exp\left(\frac{M\bar{q}_v}{R}\left(\frac{1}{T'} - \frac{1}{T''}\right)\right) \approx 0.139\ \mathrm{bar}\,,$$

which is slightly higher than the value listed in the steam table (0.137 bar; see Appendix A). Based on $p_s(T'')$, we find that the mass of vapor $m_v'' \approx 0.093$ kg and the heat supplied by the thermostat

$$m_v''\left[q_v(T'') - \frac{RT''}{M}\right] \approx 0.206\ \mathrm{MJ}\,.$$

**Problem 2.11.**

*In a thermally insulated ten-liter vessel lies a paramagnetic cuboid with a volume of* 0.1 dm$^3$ *and a heat capacity of* 10 J/K. *The vessel is surrounded by atmosphere at* 1 bar *and* 27 °C. *A valve connecting the vessel to the atmosphere is opened and left open until the pressures equalize and the air exchanges heat with the cuboid. Calculate the final temperature in the vessel! The initial temperature of the cuboid is* −173 °C; *the heat capacity ratio of air is* 7/5. *What is the answer if the process takes place in a magnetic field of strength of* $10^7$ A/m*? The magnetic susceptibility of the paramagnet is given by the Curie law* $\chi = a/T$ *with* $a = 0.1$ K.

It is best if the cuboid and the air that enters the vessel together are treated as a single system (Fig. 2.6). The work done on the system by the atmosphere is $W = pV_1'$, where $V_1'$ denotes the volume of air that enters the vessel and $p$ is the atmospheric pressure; the mass of air is $m_1'$. As a result, the internal energy of the system changes by

$$\Delta U = m_1' c_V (T - T_1') + C(T - T_2')\,,$$

where $c_V$ is the specific heat of air, $C$ is the heat capacity of the block, $T_1'$ is the temperature of the atmosphere, $T_2'$ is the initial temperature of the cuboid, and $T$ is the final temperature of the system. No heat is exchanged with the environment. From $\Delta U = W$, $c_V = R/M(\kappa - 1)$, $\kappa = c_p/c_V$, and the equations of state $pV_1' = (m_1'/M)RT_1'$ and $pV_1 = (m_1'/M)RT$ (where $V_1$ is the difference of volumes of the vessel and the cuboid) one arrives at a quadratic equation that determines $T$:

$$C\,T^2 + \left(\frac{pV_1}{\kappa - 1} - CT_2'\right) T - \frac{\kappa p V_1}{\kappa - 1} T_1' = 0.$$

The physically relevant solution is $T = -16\,°\mathrm{C}$.

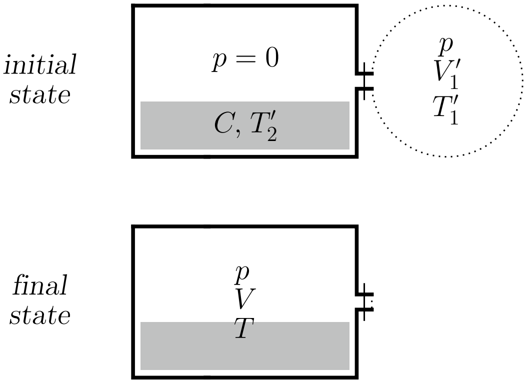

**Fig. 2.6** Air that enters the vessel and the paramagnetic cuboid in the vessel are seen as the system of interest

In a magnetic field of strength $H$, the change of the internal energy is given by the same expression as above, because $(\partial U/\partial T)_H$ does not depend on $H$. At the same time, the change of temperature of the cuboid, which is induced by the air pushed into the vessel, is accompanied by a change in its magnetization resulting in an additional (magnetic) contribution to work:

$$W_m = \int_{T_2'}^{T} \mu_0 V_2 H \, \mathrm{d}M = \mu_0 V_2 a H^2 \left( T^{-1} - T'^{-1}_2 \right) .$$

We used the Curie law $M = aH/T$ which gives $\mathrm{d}M = -(aH/T^2)\,\mathrm{d}T$; $V_2$ denotes the volume of the cuboid. Now we have $\Delta U = W + W_m$, leading to a modified quadratic equation for $T$

$$C\,T^2 + \left( \frac{pV_1}{\kappa - 1} - CT_2' + \frac{\mu_0 V_2 a H^2}{T_2'} \right) T - \left( \frac{pV_1 \kappa}{\kappa - 1} T_1' + \mu_0 V_2 a H^2 \right) = 0 \, ,$$

which gives $T = -16.3\,°\mathrm{C}$.

**Problem 2.12.**
*Water at* 40.6 bar *and* 250 °C *is pushed along a thermally insulated tube through a valve into a chamber where the pressure drops to* 10 bar. *How much water evaporates? The missing data are to be extracted from the steam table (see Appendix* A*).*

The process takes place at constant enthalpy. From the steam table we find that at 10 bar the vapor–water equilibrium is at 180 °C, which is the final temperature of the system. For this constant-enthalpy process, we have

$$m_l' h_l' = m_l h_l + m_v h_v .$$

Here $m_l'$ and $m_l$ are the initial and final mass of water, respectively, $m_v$ is the mass of vapor, whereas $h_l'$, $h_l$, and $h_v$ are the corresponding specific enthalpies. The final specific enthalpies of vapor and water, $h_v = 2778$ kJ/kg and $h_l = 763$ kJ/kg, are found in the table. On the other hand, the initial specific enthalpy of water $h_l'$ slightly exceeds the tabulated value of 1086 kJ/kg which corresponds to phase equilibrium at 39.8 bar rather than at 40.6 bar. The correction $\Delta h_l' = \Delta p/\rho_l = 102$ J/kg can be neglected, which finally leads to

$$\frac{m_v}{m_l'} = \frac{h_l' - h_l}{h_v - h_l} = 0.16.$$

# Chapter 3
# The Second Law

**Problem 3.1.**
*A calorimeter contains* 0.8 kg *of water and* 0.2 kg *of ice in equilibrium at* 0 °C. *A one-kilogram piece of iron, initially at* 100 °C, *is dropped into the water. Calculate the temperature of the system in equilibrium as well as the change of entropy of the system, assuming that thermal insulation is perfect! The heat capacity of iron is* 450 J/kgK *and that of water is* 4180 J/kgK; *the heat of fusion of ice is* 336 kJ/kg.

We denote the masses of ice and iron by $m_i$ and $m_{\mathrm{Fe}}$, respectively, and their initial temperatures by $T_0$ and $T_{\mathrm{Fe}}$. The heat required to melt all of the ice is $m_i q_f = 67.2\,\mathrm{kJ}$. On the other hand, upon cooling from 100 °C to 0 °C the piece of iron emits only $Q = m_{\mathrm{Fe}} c_p (T_{\mathrm{Fe}} - T_0) = 45$ kJ of heat. (Here $c_p$ is the specific heat of iron and $q_f$ is the heat of fusion of ice.) Thus, in the final state water and ice coexist and the final temperature is 0 °C; the mass of ice that melts is $m_l' = Q/q_f = 0.134$ kg. As the process is irreversible, the entropy change is calculated by considering a process involving reversible heat exchange that leads to the same final state:

$$\Delta S = m_{\mathrm{Fe}} c_p \int_{T_{\mathrm{Fe}}}^{T_0} \frac{\mathrm{d}T}{T} + \frac{m_l' q_f}{T_0} = 24.5\ \mathrm{J/K}\,.$$

**Problem 3.2.**
*A small piece of ice is thrown into supercooled water at* −20 °C *as a seed crystal. Calculate the fraction of water that freezes and calculate the corresponding increase of specific entropy! The heat of fusion of ice at* 0 °C *and* 1 bar *is* 336 kJ/kg; *the specific heat capacities of ice and water are* 2100 J/kgK *and* 4180 J/kgK, *respectively.*

The final temperature at a pressure of 1 bar is 0 °C. We denote the initial mass of water by $m$ and the mass of water that freezes by $m'$. Then the heat emitted upon freezing ($m' q_f$) is expended to heat the supercooled water from $T' = -20\,°\mathrm{C}$ to $T = 0\,°\mathrm{C}$, the heat required for this being given by $m c_p (T - T')$. Here $c_p$ is the

G. Skačej and P. Ziherl, *Solved Problems in Thermodynamics and Statistical Physics*, https://doi.org/10.1007/978-3-030-27661-4_3

specific heat of water and $q_f$ is the heat of fusion of ice. The fraction of water that freezes is equal to

$$x = \frac{m'}{m} = \frac{c_p(T - T')}{q_f} = 0.25\,;$$

the process is irreversible. Like in Problem 3.1, the entropy change is calculated for a suitable reversible process ending in the same final state as the original process, where the supercooled water is first reversibly heated to 0 °C and then the above fraction of water is reversibly frozen at this temperature. Therefore

$$\Delta s = \frac{\Delta S}{m} = c_p \int_{T'}^{T} \frac{\mathrm{d}T}{T} - \frac{x q_f}{T} = 11.8\ \mathrm{J/kgK}\,.$$

**Problem 3.3.**
*A thermally insulated container is partitioned into halves by a wall. The first half contains boiling water at* 130 °C, *whereas the second one is evacuated. The total volume of the container is* 5 dm$^3$. *At some point the wall breaks, and the system is allowed to reach the equilibrium state. Find the change of entropy of water! The molar mass and density of water are* 18 kg/kmol *and* 934 kg/m$^3$, *respectively; the saturated vapor pressure at* 130 °C *is* 2.7 bar *and the heat of vaporization is* 2.17 MJ/kg; *the constant-volume specific heat capacities of vapor and liquid water are* 1900 J/kgK *and* 4180 J/kgK, *respectively.*

The total mass of water is $m = \rho V/2 = 2.33$ kg; $\rho = 934$ kg/m$^3$ and $V = 5$ dm$^3$. A fraction of water of initial temperature $T = 130$ °C evaporates and fills the empty space in the container; consequently, the vapor and the remaining water cool down by $\Delta T$. One can expect that only a small fraction of water evaporates and that $\Delta T \ll T$. In this case, the vapor pressure does not differ significantly from the saturated vapor pressure $p_s$ at the initial temperature and the mass of vapor can be readily calculated by approximating it by an ideal gas, which gives $m_v = p_s VM/2RT = 3.63$ g. Upon expansion into vacuum, there is no work expended by vapor and the first law thus reads

$$m_v\left(q_v - \frac{RT}{M}\right) = m_v c_V^v\,\Delta T + (m - m_v)\,c_V^l\,\Delta T\,,$$

where $q_v$ is the heat of vaporization at 130 °C and the indices (either in subscript or superscript) refer to the state of matter: Liquid ($l$) or vapor ($v$). This gives

$$\Delta T = \frac{m_v\,(q_v - RT/M)}{m_v c_V^v + (m - m_v)\,c_V^l} \approx \frac{m_v\,(q_v - RT/M)}{m c_V^l} = 0.74\ \mathrm{K} \ll T\,.$$

We neglected the heat capacity of vapor. The entropy change is now calculated by considering a reversible process, where the boiling water is first vaporized at constant

$p_s$ and then the whole system is cooled by $\Delta T$:

$$\Delta S \approx \frac{m_v q_v}{T} + m c_V^l \ln\left(1 - \frac{\Delta T}{T}\right) = 1.65\ \text{J/K}\,.$$

Again, we assumed that $m_v c_V^v \ll m c_V^l$.

**Problem 3.4.**

*A vessel contains* 500 l *of air at* 1 bar *and* 20 °C *and a one-liter bottle filled with air at* 100 bar *and* −20 °C. *The bottle explodes. Find the final air temperature if* 8 kJ *of heat broke into the vessel from the environment during the explosion! Calculate the change of entropy of air! The heat capacity of air at constant volume is* 720 J/kgK *and the heat capacity ratio* 7/5.

Let the indices "1" and "2" denote the air in the vessel and in the bottle, respectively. Before explosion, the two masses of air are described by $p_1 V_1 = m_1 R T_1 / M$ and $p_2 V_2 = m_2 R T_2 / M$. We consider the two masses as a single system so that the first law reads $m_1 c_V (T - T_1) + m_2 c_V (T - T_2) = Q$, where $Q$ is the heat supplied by the environment. Upon inserting $m_1$ and $m_2$ expressed from the above equations of state, we find that the final temperature is given by

$$T = \frac{Q(\kappa - 1) + p_1 V_1 + p_2 V_2}{p_1 V_1 / T_1 + p_2 V_2 / T_2} = 27.7\,^\circ\text{C}.$$

The change of entropy is calculated by imagining a reversible process that brings each of the two masses of air from its initial state to the common final state, that is,

$$\Delta S = c_V \left[ m_1 \ln\left(\frac{T}{T_1}\right) + m_2 \ln\left(\frac{T}{T_2}\right)\right] + \frac{R}{M}\left[ m_1 \ln\left(\frac{V}{V_1}\right) + m_2 \ln\left(\frac{V}{V_2}\right)\right],$$

where $V = V_1 + V_2$; this gives $\Delta S = 274$ J/K. Note that this value differs from $\int \mathrm{d}Q/T$ since the process is irreversible. Here the heat $Q$ merely co-determines the final state, i.e., the final temperature.

**Problem 3.5.**

*A heat pump receives heat from a river at* 0 °C *and supplies it to a radiator at* 30 °C. *What is the minimum work needed for every joule of heat emitted by the radiator?*

We use $Q_1$ to denote the heat received by the pump at $T_1 = 0\,^\circ\text{C}$ from the river and $Q_2$ to denote the heat emitted at $T_2 = 30\,^\circ\text{C}$ by the radiator (Fig. 3.1). The work needed is $W = Q_2 - Q_1$, and from the second law for a closed cycle it follows that $Q_2/T_2 \geq Q_1/T_1$. Therefore

$$\frac{W}{Q_2} \geq 1 - \frac{T_1}{T_2} = 0.099$$

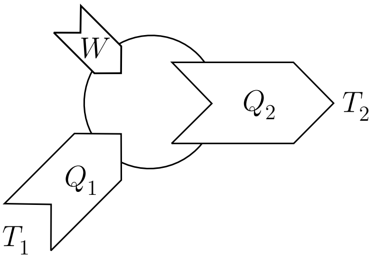

**Fig. 3.1** Energy balance of a heat pump

so that every joule of heat emitted requires at least 99 mJ of work.

### Problem 3.6.

*A refrigerator pumps heat at* 0 °C *and emits it into the environment at* 20 °C, *receiving instead of work additional heat at* 100 °C. *How much heat must the refrigerator at least receive at* 100 °C *for every joule of heat absorbed at* 0 °C*?*

Let us denote the heat emitted/received by the system at $T_i$ ($i = 0, 1, 2$; Fig. 3.2) by $Q_i$ where $T_0 = 0\,°\mathrm{C}$, $T_1 = 20\,°\mathrm{C}$, and $T_2 = 100\,°\mathrm{C}$. The first and the second laws read $Q_0 + Q_2 = Q_1$ and $Q_0/T_0 + Q_2/T_2 \leq Q_1/T_1$, respectively. It follows that

$$\frac{Q_2}{Q_0} \geq \frac{T_1^{-1} - T_0^{-1}}{T_2^{-1} - T_1^{-1}} = 0.34\,.$$

For every joule of heat absorbed at 0 °C, at least 0.34 J of heat has to be supplied to the refrigerator at 100 °C.

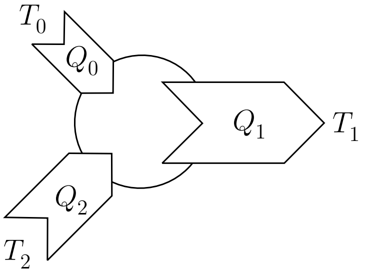

**Fig. 3.2** Energy balance of a refrigerator receiving heat instead of work

### Problem 3.7.

*An ideal heat engine operates between thermal reservoirs of finite capacities and initial temperatures of* 200 °C *and* 150 °C. *The heat capacity of each reservoir is* 5 MJ/K. *Calculate the equilibrium temperature, the total work performed by the engine, and the total change of entropy!*

We denote the initial temperatures of the reservoirs by $T_1' = 200\,°\mathrm{C}$ and $T_2' = 150\,°\mathrm{C}$, and the corresponding heat capacities by $C$. While heat is being pumped from the first to the second reservoir, the difference of the instantaneous temperatures of the reservoirs' $T_1$ and $T_2$ decreases (Fig. 3.3). In each cycle, heat $\mathrm{d}Q_1 = -C\,\mathrm{d}T_1$ is absorbed by the engine from the hotter reservoir ($\mathrm{d}T_1 < 0$) and heat $\mathrm{d}Q_2 = -C\,\mathrm{d}T_2$ ($\mathrm{d}T_2 > 0$) is emitted to the colder reservoir. As the engine is ideal $\mathrm{d}S = \mathrm{d}Q_1/T_1 + \mathrm{d}Q_2/T_2$. In each cycle we have $\mathrm{d}S = 0$ so that

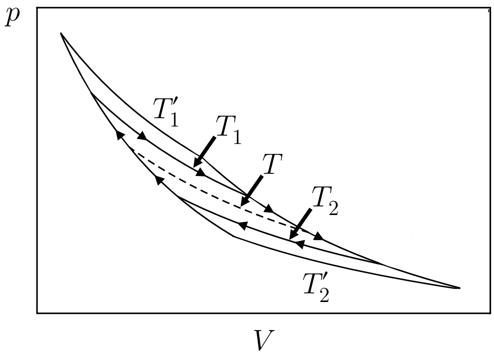

**Fig. 3.3** $pV$ diagram of an ideal heat engine operating between thermal reservoirs with finite heat capacities. The steep lines are the adiabats; they are connected by the less steep isotherms. The useful work performed by the engine decreases from cycle to cycle and when the temperatures of the reservoirs equalize, the engine ceases to operate. The diagram represents the cycle for an ideal gas

$$\int_{T_1'}^{T} \frac{\mathrm{d}T_1}{T_1} = -\int_{T_2'}^{T} \frac{\mathrm{d}T_2}{T_2}\,,$$

where $T$ stands for the final temperature. After integration we obtain

$$T = \sqrt{T_1' T_2'} = 174.3\,°\mathrm{C}\,.$$

The total useful work done by the engine is $W = -\int(\mathrm{d}Q_1 + \mathrm{d}Q_2)$ or

$$W = C\left(\int_{T_1'}^{T} \mathrm{d}T_1 + \int_{T_2'}^{T} \mathrm{d}T_2\right) = C\left(2T - T_1' - T_2'\right) = -7\,\mathrm{MJ}\,.$$

The change of entropy of the reservoirs is

$$\begin{aligned}\Delta S &= \int_{T_1'}^{T} \frac{\mathrm{d}Q_1}{T_1} + \int_{T_2'}^{T} \frac{\mathrm{d}Q_2}{T_2} \\ &= -C\left(\int_{T_1'}^{T} \frac{\mathrm{d}T_1}{T_1} + \int_{T_2'}^{T} \frac{\mathrm{d}T_2}{T_2}\right) = \ln \frac{T^2}{T_1'T_2'} = 0\,,\end{aligned}$$

which could have been guessed in advance since the engine is ideal and $\mathrm{d}S = 0$ separately in each cycle.

**Problem 3.8.**
*An ideal heat pump absorbs heat from a superconducting sample, initially at* 10 K, *and pumps it into a thermal reservoir held at a constant temperature of* 12 K. *Find the amount of heat pumped into the reservoir by the time the sample cools down to* 3 K*! How much work is expended in the process? Initially the sample is in the normal phase, whereas at a critical temperature of* 7 K *it exhibits a second-order transition into the superconducting phase. The heat capacities of the sample in the normal and superconducting phase are* $C_N(T) = bT^3 + cT$ *and* $C_S(T) = aT^3$, *respectively, where* $a = 10^{-5}$ J/K$^4$, $b = 8 \times 10^{-6}$ J/K$^4$, *and* $c = 6 \times 10^{-6}$ J/K$^2$.

In each cycle, the heat absorbed is $\mathrm{d}Q_1 = -C_i(T_1)\mathrm{d}T_1$, where $T_1$ is the temperature of the sample and the index $i = N, S$ denotes the normal and the superconducting state depending on $T_1$. In a cooling process that starts at $T'$ and continues beyond the critical temperature $T_c$ to the final state at $T$, the total heat absorbed reads

$$\begin{aligned}Q_1 &= \int \mathrm{d}Q_1 = -\int_{T'}^{T_c} C_N(T_1)\mathrm{d}T_1 - \int_{T_c}^{T} C_S(T_1)\mathrm{d}T_1 \\ &= -\frac{a}{4}\left(T^4 - T_c^4\right) - \frac{b}{4}\left(T_c^4 - T'^4\right) - \frac{c}{2}\left(T_c^2 - T'^2\right) = 21.1\ \mathrm{mJ}\,.\end{aligned}$$

(Note that since the normal–superconductor transition is continuous, there is no latent heat associated with it.) If we denote the heat emitted to the reservoir in each cycle by $\mathrm{d}Q_0$ and the constant temperature of the reservoir by $T_0$, the second law states that $\mathrm{d}Q_0/T_0 + \mathrm{d}Q_1/T_1 = 0$. Thus, the total heat pumped into the reservoir is given by

$$\begin{aligned}Q_0 &= -T_0 \int \frac{\mathrm{d}Q_1}{T_1} = T_0\left(\int_{T'}^{T_c} \frac{C_N(T_1)\mathrm{d}T_1}{T_1} + \int_{T_c}^{T} \frac{C_S(T_1)\mathrm{d}T_1}{T_1}\right) \\ &= T_0\left[\frac{a}{3}\left(T^3 - T_c^3\right) + \frac{b}{3}\left(T_c^3 - T'^3\right) + c\left(T_c - T'\right)\right] = -33.9\ \mathrm{mJ}.\end{aligned}$$

The total work expended in the process is $-Q_0 - Q_1 = 12.8$ mJ.

**Problem 3.9.**
*The cycle of a heat engine consists of two adiabats and of two isobars. Calculate the ratio of the highest and the lowest pressure in the engine if its efficiency is to be* 0.43*! The heat capacity ratio of the working fluid is* $7/5$.

Heat is supplied to the working fluid only along the top isobar at $p_2$, which starts at temperature $T_2$ and ends at $T_3 > T_2$; this heat is equal to $Q_i = mc_p(T_3 - T_2)$ (Fig. 3.4). The working fluid emits heat only along the bottom isobar at $p_1$ going from $T_4$ to $T_1 < T_4$; the heat emitted is $Q_o = mc_p(T_1 - T_4)$. As each of the two adiabats connects the same pair of isobars, we have

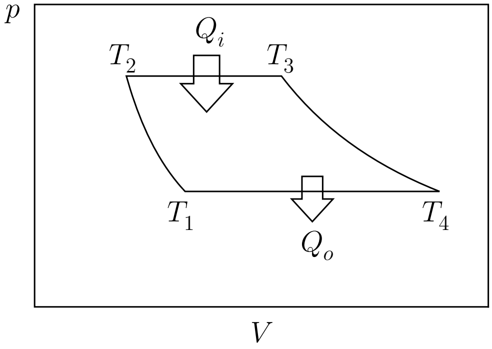

**Fig. 3.4** $pV$ diagram of a cycle consisting of two adiabats and two isobars

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{1-1/\kappa} = \frac{T_3}{T_4}\,.$$

The efficiency of the heat engine is equal to

$$\eta = \frac{Q_i + Q_o}{Q_i} = 1 - \frac{T_4 - T_1}{T_3 - T_2} = 1 - \frac{T_4}{T_3} = 1 - \left(\frac{p_1}{p_2}\right)^{1-1/\kappa}\,,$$

which gives

$$\frac{p_2}{p_1} = (1-\eta)^{-\kappa/(\kappa-1)} = 7.15\,.$$

### Problem 3.10.

*An ideal refrigerator pumps heat from a thermal reservoir with an infinite heat capacity at* 0 °C *and emits it to a second reservoir with a heat capacity denoted by* $C_1$ *and an initial temperature of* 20 °C. *Instead of work, the refrigerator absorbs additional heat from a third reservoir with a heat capacity denoted by* $C_2$ *and an initial temperature of* 100 °C. *After operating for a period of time, the temperatures of the second and the third reservoir equalize at* 40 °C. *Find the ratio* $C_2/C_1$*! How much heat is pumped from the first reservoir until temperatures of the second and third reservoir equalize if* $C_2 = 5\ \mathrm{kJ/K}$*?*

Let us denote the instantaneous temperatures of the first, second, and third reservoir by $T_0$, $T_1$, and $T_2$, respectively. The initial temperatures of the second and third reservoir are $T_1' = 20\,^\circ\text{C}$ and $T_2' = 100\,^\circ\text{C}$, whereas the temperature of the first one remains constant at $T_0 = 0\,^\circ\text{C}$. In each cycle, the refrigerator receives heat from the first and the third reservoir ($\mathrm{d}Q_0$ and $\mathrm{d}Q_2 = -C_2\,\mathrm{d}T_2$, respectively) and supplies heat to the second reservoir ($\mathrm{d}Q_1 = -C_1\,\mathrm{d}T_1$): $\mathrm{d}Q_0 + \mathrm{d}Q_1 + \mathrm{d}Q_2 = 0$. At the same time, the second law states that $\mathrm{d}Q_0/T_0 + \mathrm{d}Q_1/T_1 + \mathrm{d}Q_2/T_2 = 0$, yielding

$$\frac{\mathrm{d}Q_2}{\mathrm{d}Q_1} = \frac{C_2\,\mathrm{d}T_2}{C_1\,\mathrm{d}T_1} = \frac{T_1^{-1} - T_0^{-1}}{T_0^{-1} - T_2^{-1}}\,.$$

Once $T_1$ and $T_2$ become equal, we have $\mathrm{d}Q_1 = -\mathrm{d}Q_2$ and hence $\mathrm{d}Q_0 = -\mathrm{d}Q_1 - \mathrm{d}Q_2 = 0$: Beyond this point, no heat is pumped from the first reservoir anymore. The above equation is rearranged and integrated from $T_1$ and $T_2$ to the final temperature $T$ to obtain

$$\frac{C_2}{C_1} = -\frac{T_0\ln(T/T_1') - T + T_1'}{T_0\ln(T/T_2') - T + T_2'} = 0.163\,.$$

The total heat absorbed from the first reservoir is now equal to $C_2(T - T_2') + C_1(T - T_1') = 314$ kJ.

**Problem 3.11.**

*A Carnot heat engine uses an ideal monatomic gas as the working fluid and operates between temperatures $T_0$ and $T_1 = 4T_0$. The highest-to-lowest gas volume ratio in the cycle is $V_1/V_0 = 64$. By what factor does the work done by the engine per cycle increase or decrease if the working fluid is replaced by an ideal diatomic gas? The number of moles of the gas as well as $T_0$, $T_1$, $V_0$, and $V_1$ remain unchanged; the heat capacity ratios $c_p/c_V$ for a monatomic and diatomic gas are $5/3$ and $7/5$, respectively.*

Since the efficiency of the Carnot engine depends only on temperatures $T_0$ and $T_1$, it remains unaltered upon changing the working fluid. The ratio of the work done by a diatomic gas and a monatomic gas $W_2/W_1$ is, therefore, equal to the ratio of the respective amounts of heat supplied along the hotter isotherm $Q_2/Q_1$. On the $pV$ diagram (Fig. 3.5), the hotter isotherm extends to $V''$ in the case of the monatomic gas but only to $V' < V''$ in the case of the diatomic gas; consequently $Q_2 = (m/M)RT_1\ln(V'/V_0)$ and $Q_1 = (m/M)RT_1\ln(V''/V_0)$ are not equal.

The volumes $V'$ are $V''$ related through the equations of the adiabatic process $T_1V''^{\kappa_1-1} = T_0V_1^{\kappa_1-1}$ and $T_1V'^{\kappa_2-1} = T_0V_1^{\kappa_2-1}$, where $\kappa_1$ and $\kappa_2$ are the corresponding heat capacity ratios. It follows that

$$\frac{W_2}{W_1} = \frac{\ln(V_1/V_0) + (\kappa_2 - 1)^{-1}\ln(T_0/T_1)}{\ln(V_1/V_0) + (\kappa_1 - 1)^{-1}\ln(T_0/T_1)} = \frac{1}{3}\,.$$

A diatomic gas apparently provides less useful work in each cycle because the slope of the adiabats is lower than for the monatomic gas.

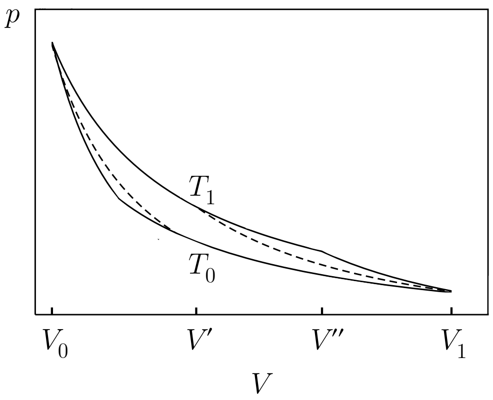

**Fig. 3.5** $pV$ diagrams of a Carnot heat engine operating between the same two isotherms and between the same largest and smallest volume using a monatomic gas (solid line) and a diatomic gas (dashed line). For a diatomic gas, the surface area enclosed by the isotherms and adiabats—and thus the work done in each cycle—is smaller than for the monatomic gas

## Problem 3.12.

*A steam engine executes the following cycle: Water at* $60\,^\circ\mathrm{C}$ *is first isothermally compressed to* $4.76$ bar, *then heated to the boiling point at* $150\,^\circ\mathrm{C}$ *and evaporated at constant pressure. Next, steam enters a cylinder where it is adiabatically expanded to* $60\,^\circ\mathrm{C}$, *and then it is pushed by the piston into the condenser where it condenses at* $60\,^\circ\mathrm{C}$. *Calculate the efficiency of this engine given that it operates reversibly! Compare it to the efficiency of a Carnot engine operating between the same extreme temperatures!*

The diagram of the cycle is shown in Fig. 3.6. The heat exchange balance includes these contributions:

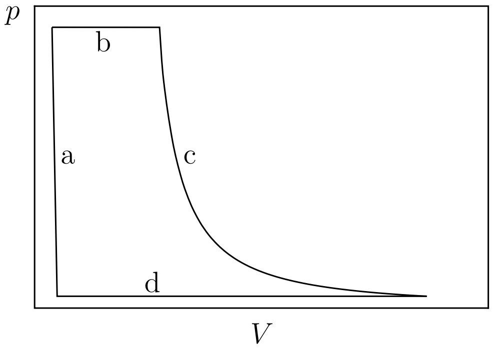

**Fig. 3.6** $pV$ diagram of a steam engine: The compression of water (**a**) is followed by isobaric heating and evaporation (**b**), by adiabatic expansion and partial steam condensation (**c**), and finally, by a complete steam condensation (**d**)

- Upon isothermal compression at $T_1 = 60\,^\circ\mathrm{C}$, from $p_1 = p_s(60\,^\circ\mathrm{C}) = 0.20$ bar to $p_2 = p_s(150\,^\circ\mathrm{C}) = 4.76$ bar water emits $Q/m = (T_1/m)\int_{p_1}^{p_2}(\partial S/\partial p)_T\,\mathrm{d}p = -T_1\beta(T_1)(p_2 - p_1)/\rho_l(T_1) = -81$ J/kg of heat. Here $\rho_l^{-1}(T_1) = 1.0171$ dm$^3$/kg is the specific volume of water and $\beta(T_1) = 5.22 \times 10^{-4}$ K$^{-1}$ is the volumetric thermal expansion coefficient.
- To heat water from $T_1$ to $T_2$ at 4.76 bar requires $c_p(T_2 - T_1) = 378$ kJ/kg of heat.
- From the steam tables, we find that evaporation of water at $T_2$ requires $\Delta h(T_2) = 2114.4$ kJ/kg of heat.
- Upon adiabatic expansion of steam, $s_v(T_2, p_2) = x s_v(T_1, p_1) + (1 - x)s_l(T_1, p_1)$, where $x$ stands for the steam fraction in the partially condensed mixture. From the steam table (Appendix A), it is found that the specific entropy of steam at $p_2$ and $T_2$ is equal to $s_v(T_2, p_2) = 6.84$ kJ/kgK, whereas the specific entropies of steam and water at $p_1$ and $T_1$ are $s_v(T_1, p_1) = 7.91$ kJ/kgK and $s_l(T_1, p_1) = 0.83$ kJ/kgK, respectively. It follows that

$$x = \frac{s_v(T_2, p_2) - s_l(T_1, p_1)}{s_v(T_1, p_1) - s_l(T_1, p_1)} = 0.849\,.$$

  During this stage, the working fluid neither receives nor emits any heat.
- During the final condensation stage at $T_1$, the heat emitted by steam and water equals $x\,\Delta h(T_1) = 0.849 \times (-2358$ kJ/kg$) = -2001$ kJ/kg.

The total heat received by the engine is thus $Q_i = 2458$ kJ/kg, whereas the total heat emitted is $Q_o = -2001$ kJ/kg. The efficiency of the steam engine is then

$$\eta = \frac{Q_i + Q_o}{Q_i} = 0.196\,.$$

The efficiency of a Carnot engine operating between the same extreme temperatures is 0.213. The performance of the steam engine apparently closely approaches that of the Carnot cycle.

**Problem 3.13.**

*A mixture of* 50% *water and* 50% *steam is adiabatically compressed from* 1 bar *to* 7 bar *and released through a thermally insulated nozzle back to the chamber where a constant pressure of* 1 bar *is maintained. Find the mass fraction of steam after two cycles! How many cycles are needed to obtain just one component? Use the data from the steam table (see Appendix A).*

During the first stage of the cycle, entropy is constant. If we denote the mass fraction of steam before and after the adiabatic process by $x''$ and $x'$, respectively, the constant-entropy condition reads $x''s_v'' + (1 - x'')s_l'' = x's_v' + (1 - x')s_l'$, where $s_v' = 6.708$ kJ/kgK and $s_v'' = 7.35$ kJ/kgK stand for the specific entropies of steam at 7 bar and 1 bar, respectively, whereas $s_l' = 1.99$ kJ/kgK and $s_l'' = 1.31$ kJ/kgK are the respective specific entropies of water. Then we have

$$x' = \frac{s_l'' - s_l' + (s_v'' - s_l'')x''}{s_v' - s_l'}\,.$$

In the second stage, enthalpy is constant, yielding $x'h'_v + (1 - x')h'_l = xh''_v + (1 - x)h''_l$. Here $x$ denotes the steam fraction just after the isenthalpic process; the notation used for the specific enthalpies $h'_v = 2764$ kJ/kg, $h''_v = 2676$ kJ/kg, $h'_l = 697$ kJ/kg, and $h''_l = 419$ kJ/kg is analogous to that for the specific entropies. Therefore

$$x = \frac{h'_l - h''_l + (h'_v - h'_l)x'}{h''_v - h''_l}\,.$$

The fraction of steam before and after each stage is tabulated below for the first five cycles:

| $cycle$ | $x''$ | $x'$ | $x$ |
|---|---|---|---|
| 1 | 0.500 | 0.496 | 0.577 |
| 2 | 0.577 | 0.595 | 0.668 |
| 3 | 0.668 | 0.711 | 0.775 |
| 4 | 0.775 | 0.848 | 0.900 |
| 5 | 0.900 | 1.009 | |

The table shows that after the adiabatic stage of the fifth cycle, no water is left in the system.

**Problem 3.14.**

*A thermostat at* 20 °C *contains a cylinder divided into two equal compartments by a heavy piston of mass of* 1 kg. *The compartments are filled with air at* 1 bar. *The cylinder is rotated from its initial horizontal position around the center of mass into the vertical position. Calculate the change of entropy of the system if the diameter of the cylinder is* 5 cm *and the initial volume of each compartment is* 1 l*! The piston is well sealed.*

The air in the lower compartment is isothermally compressed as the cylinder is rotated, and its pressure is increased from the initial value of $p$ to $p_2$; at the same time, the air in the upper compartment is isothermally expanded so that its pressure drops from $p$ to $p_1$. The final volumes of the compartments are determined by mechanical equilibrium, $p_2 - p_1 = p_p$, where $p_p = mg/\pi r^2$ is the pressure due to the force of gravity of the piston; $r$ denotes the radius of the cylinder. As the process is isothermal, the above condition can be rewritten as $pV/V_2 - pV/V_1 = p_p$. The total volume of the cylinder does not change upon rotation or $V_1 + V_2 = 2V$, where $V$ is the initial volume of each compartment. From these equations we obtain

$$\frac{1}{2}\left(\frac{V_1}{V}\right)^2 + \left(\frac{p}{p_p} - 1\right)\frac{V_1}{V} - \frac{p}{p_p} = 0\,.$$

The solution reads $V_1 = V\left[1 - p/p_p + \sqrt{1 + (p/p_p)^2}\right] = 1.025$ l, immediately yielding $V_2 = 0.975$ l.

Since the rotation is carried out around the center of mass, no work is performed by gravity. The process is isothermal, so the heat exchanged by the air in each compartment with the thermostat is equal to minus the work expended. Consequently, $\Delta S = -(W_1 + W_2)/T$, with $W_i = -\int_V^{V_i} p_i \,\mathrm{d}V_i = -pV \ln(V_i/V)$. Finally we obtain

$$\Delta S = \frac{pV}{T} \ln\!\left(2(p/p_p)\left[\sqrt{1 + (p/p_p)^2} - (p/p_p)\right]\right) = -0.213\ \mathrm{mJ/K}\,.$$

**Problem 3.15.**

*A stage in a heat engine cycle is represented by a polytropic process $pV^n = const.$, where $n = 1.1$. For such a process, calculate the heat capacity of air used as the working fluid! Find the change of entropy of 1 kg of air during this process if the temperature rises from 50 °C to 100 °C! The specific heat at constant volume is 723 J/kgK and the heat capacity ratio is 7/5.*

The heat that the air exchanges with the environment during the polytropic process is calculated using the first law: $Q = \Delta U - W$. By definition, the change of internal energy is given by $\Delta U = mc_V(T - T')$, where $T$ and $T'$ are the final and the initial temperature of the air, respectively. The work done is equal to

$$W = -\int_{V'}^{V} p\,\mathrm{d}V = \frac{p'V'^n}{n-1}\left(V^{1-n} - V'^{1-n}\right) = \frac{mR}{(n-1)M}\left(T - T'\right),$$

where we assumed that the air is an ideal gas. The heat exchanged with the environment is then

$$Q = m\left(c_V - \frac{R/M}{n-1}\right)\left(T - T'\right) = mc_V\frac{n-\kappa}{n-1}\left(T - T'\right),$$

where we took into account that $R/M = c_p - c_V$ and $\kappa = c_p/c_V$. Finally we have

$$c_n = \frac{1}{m}\frac{\mathrm{d}Q}{\mathrm{d}T} = \frac{n-\kappa}{n-1}c_V = -2169\ \mathrm{J/kgK}\,.$$

One readily observes that $c_n$ is negative for all $n$ within the range between 1.0 and $\kappa$. For these values of $n$, the work expended by the working fluid during the polytropic expansion exceeds the heat absorbed, which results in a decrease of the internal energy and thus in a decrease of temperature. Let us also mention that the obtained $c_n$ includes a number of well-known processes:

- $n = 0$ corresponds to an isobaric process and gives $c_n = \kappa c_V = c_p$;
- $n = 1$ describes an isothermal process where $c_n \to \pm\infty$;
- $n = \kappa$ for an adiabatic process with $c_n = 0$; and
- $n \to \infty$ represents an isochoric process, yielding $c_n = c_V$.

The dependence of the heat capacity on exponent $n$ is depicted in Fig. 3.7.

Finally, we calculate the change of entropy for a polytropic process with $n = 1.1$ where the air is heated from 50 °C to 100 °C:

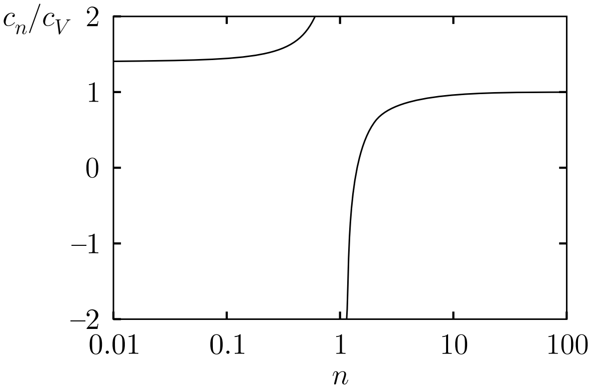

**Fig. 3.7** Heat capacity for a gas undergoing a polytropic process $pV^n = const.$ as a function of $n$ plotted for $\kappa = 1.4$. The limits $n = 0$ and $n \to \infty$ correspond to an isobaric and an isochoric process, respectively; $n = 1$ represents an isothermal process, and for $n = 1.4$ the process is adiabatic. For $n$ between 1 and 1.4, $c_n < 0$

$$\Delta s = \frac{\Delta S}{m} = \int_{T'}^{T} \frac{c_n}{T} \mathrm{d}T = \frac{n-\kappa}{n-1} c_V \ln \frac{T}{T'} = -312\ \mathrm{J/kgK}\,.$$

**Problem 3.16.**

*In a heat engine, photon gas is subject to a reversible thermodynamic cycle consisting of two isobars and two isochores. Calculate the efficiency of the cycle if the highest-to-lowest volume ratio is equal to 3 and the highest-to-lowest pressure ratio is 2! The density of the internal energy of the photon gas at a temperature $T$ is given by $u = 4\sigma T^4/c$, where $\sigma$ denotes the Stefan constant and $c$ is the speed of light. The pressure of the photon gas is equal to $u/3$.*

The internal energy of the photon gas is given by $U(T, V) = 4\sigma T^4 V/c$. The pressure of the gas depends only on temperature, $p(T) = 4\sigma T^4/3c$, and thus the two isobars at pressures $p_1$ and $p_2 > p_1$ correspond to isotherms at temperatures $T_1$ and $T_2 > T_1$, respectively. We denote the minimum and the maximum volume by $V_1$ and $V_2$, respectively. The efficiency of a heat engine is defined by $\eta = 1 + Q_o/Q_i$, where $Q_i$ is the heat supplied to the photon gas in the cycle and $Q_o$ is the heat emitted into the environment. Now

$$Q_i = \frac{4\sigma}{c}(T_2^4 - T_1^4)V_1 + \frac{4\sigma}{c}T_2^4(V_2 - V_1) + \frac{4\sigma}{3c}T_2^4(V_2 - V_1)\,,$$

where the first term is the heat supplied upon isochoric heating, consisting merely of the change of internal energy since no work is expended, and the remaining two terms represent the heat supplied during isobaric expansion; the second term is the change of internal energy and the third term the work expended. Analogously, the total heat emitted during the remaining two steps—isochoric cooling and isobaric compression—reads

$$Q_o = -\frac{4\sigma}{c}(T_2^4 - T_1^4)V_2 - \frac{4\sigma}{c}T_1^4(V_2 - V_1) - \frac{4\sigma}{3c}T_1^4(V_2 - V_1)\,.$$

Thus, we find that the efficiency reads

$$\eta = 1 - \frac{v(t-1) + (4/3)(v-1)}{t - 1 + (4/3)t(v-1)} = 0.105\,,$$

where $v = V_2/V_1$ and $t = (T_2/T_1)^4 = p_2/p_1$.

**Problem 3.17.**
*The highest and the lowest pressure in a Carnot engine that uses the photon gas as the working substance are* $2 \times 10^{-5}$ Pa *and* $1.2 \times 10^{-5}$ Pa, *respectively. Calculate the efficiency of the engine!*

Regardless of the working substance and its equation of state, the Carnot cycle consists of two isotherms and two adiabats, and is reversible. Hence, a step-by-step analysis of the cycle is not necessary as one can immediately apply the well-known result for the efficiency of the cycle: $\eta = 1 - T_1/T_2 = 1 - (p_1/p_2)^{1/4} = 0.12$ . Here we took into account that in a photon gas $p(T) = 4\sigma T^4/3c$; indices "1" and "2" refer to the lower and the higher isotherm and isobar, respectively.

# Chapter 4
# Thermodynamic Potentials

**Problem 4.1.**
*One kilogram of mercury is compressed isothermally at* 300 K *from* 0 *to* $10^3$ bar. *Calculate the corresponding change of internal energy* $\Delta U$*! Does the sign of* $\Delta U$ *depend on the final pressure? The density of mercury is* $13600\ \mathrm{kg/m^3}$, *its volumetric thermal expansion coefficient* $1.81 \times 10^{-4}\ \mathrm{K^{-1}}$, *and isothermal compressibility* $3.9 \times 10^{-11}\ \mathrm{Pa^{-1}}$.

The thermodynamic description of the system is based on two pairs of conjugate variables: Temperature and entropy ($T$ and $S$) and pressure and volume ($p$ and $V$). The first law reads $\Delta U = W + Q$. The work received during compression is $W = -\int_0^p p\,\mathrm{d}V$, and by taking into account $\mathrm{d}V = -\chi_T V \mathrm{d}p$ with $V = m/\rho$ we obtain

$$W = \frac{m\chi_T p^2}{2\rho} = 14.3\ \mathrm{J}\,;$$

$\rho$ and $\chi_T$ denote the density and the isothermal compressibility of the sample, respectively. The heat exchanged upon reversible compression is given by $Q = \int_0^p T(\partial S/\partial p)_T\,\mathrm{d}p$, where the Maxwell relation $(\partial S/\partial p)_T = -(\partial V/\partial T)_p = -\beta V$ is to be used; $\beta$ stands for the volumetric thermal expansion coefficient. For $T = 300$ K and $p = 10^3$ bar we have

$$Q = -\frac{m\beta T p}{\rho} = -399\ \mathrm{J}\,.$$

The internal energy decreases by $\Delta U = W + Q = -385$ J. Note that work received $W \propto p^2$ and the heat emitted $Q \propto p$. Thus at a high enough pressure, $|W| > |Q|$ and consequently $\Delta U > 0$. The threshold pressure $p'$ where the internal energy difference $\Delta U$ changes sign is given by

G. Skačej and P. Ziherl, *Solved Problems in Thermodynamics and Statistical Physics*, https://doi.org/10.1007/978-3-030-27661-4_4

$$p' = \frac{2\beta T}{\chi_T} = 2.78 \times 10^4\,\mathrm{bar}\,.$$

**Problem 4.2.**

*In the cadmium galvanic cell, voltage varies with temperature as*

$$\phi(T) = \phi_0 + a(T - T_0) + b(T - T_0)^2\,,$$

*where* $T_0 = 20\,°\mathrm{C}$, $\phi_0 = 1.0183\ \mathrm{V}$, $a = -4.06 \times 10^{-5}\ \mathrm{V/K}$, *and* $b = -0.95 \times 10^{-6}\ \mathrm{V^2/K^2}$. *By how much does the internal energy of the cell change after an electric charge of* 1 As *is reversibly passed though it at a constant temperature of* 20 °C*? What is the result if instead the process takes place in a thermally insulated cell and its heat capacity at a constant charge is* 4.2 J/K*? Thirdly, what is the change of cell temperature if the terminals are short-circuited and the amount of charge passed is* 1 As*? Finally, calculate the difference of heat capacities of the cell at constant voltage and charge!*

The pairs of thermodynamic variables of the system are temperature and entropy ($T$ and $S$) and voltage and charge ($\phi$ and $e$). The first law states that $\mathrm{d}U = T\,\mathrm{d}S + \phi\,\mathrm{d}e$. We are interested in the change of internal energy upon isothermal charge transfer, i.e., in $\Delta U \approx (\partial U/\partial e)_T\,\Delta e$, at $T_0 = 20$ °C. By taking into account the Maxwell relation $(\partial S/\partial e)_T = -(\partial \phi/\partial T)_e$, we find that

$$\left(\frac{\partial U}{\partial e}\right)_T = \left[T\left(\frac{\partial S}{\partial e}\right)_T + \phi\right]_{T=T_0} = -aT_0 + \phi_0$$

and therefore

$$\Delta U = (\phi_0 - aT_0)\,\Delta e = 1.0\,\mathrm{J}\,.$$

The first term corresponds to the electric work, whereas the second one is the heat exchanged.

On the other hand, charge transfer though a thermally insulated cell is an adiabatic process, and we are interested in $\Delta T \approx (\partial T/\partial e)_S\,\Delta e$. The derivative in question is extracted from the total differential $\mathrm{d}S = (\partial S/\partial T)_e\,\mathrm{d}T + (\partial S/\partial e)_T\,\mathrm{d}e$:

$$\left(\frac{\partial T}{\partial e}\right)_S = -\left(\frac{\partial S}{\partial e}\right)_T \Big/ \left(\frac{\partial S}{\partial T}\right)_e = \left(\frac{\partial \phi}{\partial T}\right)_e \frac{T}{C_e}\,.$$

Here we used the Maxwell relation mentioned above and we introduced the heat capacity at constant charge $C_e = T(\partial S/\partial T)_e$. This gives

$$\Delta T = \frac{aT_0}{C_e}\,\Delta e = -2.8 \times 10^{-3}\,\mathrm{K}\,.$$

The short-circuit process is analogous to the so-called Hirn experiment in a gas as $\Delta U = 0$: Since there is no electric load, the cell expends no work; at the same time, the process is fast and no heat is exchanged. From the total differential $\mathrm{d}U$ we obtain

$$\left(\frac{\partial T}{\partial e}\right)_U = -\left(\frac{\partial U}{\partial e}\right)_T \bigg/ \left(\frac{\partial U}{\partial T}\right)_e = \frac{aT_0 - \phi_0}{C_e} = -0.24\ \mathrm{K/As}\,.$$

The numerator contains the answer to the first question and the denominator is equal to $C_e = (\partial U/\partial T)_e$ by definition.

To calculate the difference of heat capacities, we assume that the system is described by an equation of state $e = e(T, \phi)$ and that $S = S\big(T, e(T, \phi)\big)$. This gives

$$C_\phi = T\left(\frac{\partial S}{\partial T}\right)_\phi = T\left[\left(\frac{\partial S}{\partial T}\right)_e + \left(\frac{\partial S}{\partial e}\right)_T \left(\frac{\partial e}{\partial T}\right)_\phi\right].$$

Upon inserting the definition of $C_e$ and the same Maxwell relation as above we find that

$$C_\phi - C_e = -T\left(\frac{\partial \phi}{\partial T}\right)_e \left(\frac{\partial e}{\partial T}\right)_\phi .$$

If we assume that for cadmium cells $e \neq e(T)$ then $C_\phi = C_e$.

**Problem 4.3.**
*Calculate the relative decrease of volume of a* $\mathrm{CS_2}$ *sample after it is placed in a capacitor and exposed to an electric field of* $6 \times 10^6\ \mathrm{V/m}$, *given that pressure and temperature are constant! Use the Clausius–Mossotti relation* $(\epsilon - 1)/(\epsilon + 2) = \rho C(T)$, *where* $\rho$ *is sample density,* $\epsilon$ *is its relative permittivity, and* $C(T)$ *is a temperature-dependent constant. Assume that at a given temperature* $\epsilon = 3$ *and that isothermal compressibility is equal to* $10^{-9}\ \mathrm{Pa}^{-1}$*!*

The three pairs of conjugate thermodynamic variables of interest are temperature and entropy ($T$ and $S$), pressure and volume ($p$ and $V$), and electric field strength and electric polarization ($E$ and $P$). The first law reads $\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + V_0 E\,\mathrm{d}P$, where $V_0$ is the (constant) capacitor volume. (Note that volume changes are measured by the rise or drop of the level of fluid $\mathrm{CS_2}$ in a capillary outside the capacitor; the volume of the fluid exposed to $E$ is thus constant and equal to $V_0$ at all times.) We need to calculate $\Delta V = \int_0^E (\partial V/\partial E)_{T,p}\,\mathrm{d}E$, which involves a derivative given by a Maxwell relation that is obtained from the thermodynamic potential $G' = U - TS + pV - V_0 PE$:

$$\left(\frac{\partial V}{\partial E}\right)_{T,p} = -V_0\left(\frac{\partial P}{\partial p}\right)_{T,E} = -V_0\epsilon_0 E\left(\frac{\partial \epsilon}{\partial p}\right)_{T,E},$$

in the last step, we used the equation of state $P = (\epsilon - 1)\epsilon_0 E$. By taking the logarithm of the Clausius–Mossotti relation and differentiating it at $T = const.$ we find that

$$\left(\frac{1}{\epsilon - 1} - \frac{1}{\epsilon + 2}\right) \mathrm{d}\epsilon = \frac{\mathrm{d}\rho}{\rho} = \chi_T \, \mathrm{d}p \, ,$$

where we used the $pVTE$ equation of state $\mathrm{d}V = V(\beta \, \mathrm{d}T - \chi_T \, \mathrm{d}p) + (\partial V/\partial E)_{T,p}$ $\mathrm{d}E$ with $\mathrm{d}T = 0$ and $\mathrm{d}E = 0$; $\beta$ and $\chi_T$ stand for the volumetric thermal expansion coefficient and the isothermal compressibility of the sample, respectively. We now get $(\partial\epsilon/\partial p)_{T,E} = \chi_T(\epsilon - 1)(\epsilon + 2)/3$ and finally

$$\frac{\Delta V}{V_0} = -\frac{1}{6}\chi_T(\epsilon - 1)(\epsilon + 2)\epsilon_0 E^2 = -5.3 \times 10^{-7}.$$

### Problem 4.4.

*Nitrogen, initially at* 2 bar *and* 20 °C, *flows through a thermally insulated valve into a vessel where the pressure of* 1 bar *is maintained. Find the change of temperature of nitrogen in this process! What would be the temperature change if the process were adiabatic and reversible? In what temperature range is the Joule–Kelvin coefficient* $(\partial T/\partial p)_H$ *negative? Use the van der Waals equation of state with the critical parameters* $p_c = 33.9$ bar *and* $T_c = -146.9\,^\circ$C*!*

From the first law it follows that in the process in question, enthalpy is conserved (Fig. 4.1). One needs to calculate $(\partial T/\partial p)_H$. In a non-ideal gas the enthalpy depends both on temperature and on pressure and thus this coefficient is nonzero. From $\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p$ and $(\partial S/\partial p)_T = -(\partial V/\partial T)_p = -\beta V$ it follows that $(\partial H/\partial p)_T = V(1 - \beta T)$, whereas from the condition that enthalpy be conserved $\mathrm{d}H = mc_p \, \mathrm{d}T + (\partial H/\partial p)_T \, \mathrm{d}p = 0$ one has

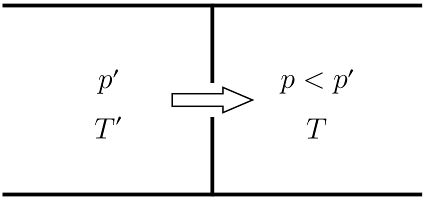

**Fig. 4.1** Joule–Kelvin process: A temperature change is observed only if the gas is not ideal

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{\beta T - 1}{\rho c_p} \, .$$

To describe the non-ideal gas, we use the virial equation of state $pV = (m/M)[RT + B_2(T)p]$ and differentiate it at $p = const.$ to obtain the volumetric thermal expansion coefficient:

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{m}{VM}\left(\frac{R}{p} + \frac{\mathrm{d}B_2}{\mathrm{d}T}\right).$$

The virial coefficient $B_2(T)$ is extracted from the lowest order comparison of the virial and van der Waals equation of state: $B_2(T) = b - a/RT$. The Joule–Kelvin coefficient, hence, reads

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{1}{Mc_p}\left(T\frac{\mathrm{d}B_2}{\mathrm{d}T} - B_2\right) = \frac{1}{Mc_p}\left(\frac{2a}{RT} - b\right).$$

The parameters of the van der Waals equation of state $a$ and $b$ can be expressed using the critical pressure $p_c = a/27b^2$ and the critical temperature $T_c = 8a/27bR$ (Problem 1.1). The so-called inversion temperature where the Joule–Kelvin coefficient changes sign is equal to

$$T_i = \frac{2a}{Rb} = \frac{27}{4}T_c = 852\ \mathrm{K}.$$

For $T < T_i$ and $\Delta p < 0$ the gas is cooled in the Joule–Kelvin process and the opposite holds for $T > T_i$. In our case, the fluid in question is a diatomic gas and thus $c_p = 7R/2M$. The change of temperature is

$$\Delta T \approx \frac{1}{Mc_p}\left(\frac{2a}{RT} - b\right)\Delta p = -0.25\ \mathrm{K}.$$

A reversible adiabatic process results in a much larger temperature change: From $\mathrm{d}S = \left(mc_p/T\right)\mathrm{d}T - \beta V\,\mathrm{d}p = 0$ we have

$$\left(\frac{\partial T}{\partial p}\right)_S = \frac{\beta T}{\rho c_p} \approx \frac{1}{\rho c_p}$$

which gives $\Delta T \approx -52.6$ K.

**Problem 4.5.**
*Show that in gases where the internal energy is independent of volume, the heat capacity at constant volume can only be a function of temperature!*

If $U \neq U(V)$, we have $(\partial U/\partial V)_T = 0$ and therefore

$$m\left(\frac{\partial c_V}{\partial V}\right)_T = \left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T\right)_V = 0$$

so that $c_V \neq c_V(V)$.

**Problem 4.6.**
*Does the heat capacity at constant volume in a van der Waals gas depend on volume? Calculate the difference between the heat capacities at constant pressure and at*

*constant volume! What is the form of the internal energy as a function of temperature and volume, assuming that the heat capacity at constant volume does not depend on temperature? Find the equation relating temperature and volume in a reversible adiabatic process!*

Usually, the van der Waals equation of state is written per kilomole of substance; here we stick to this practice and give all extensive thermodynamic quantities per kilomole, which is emphasized by subscript $M$. From the van der Waals equation of state $(p + a/V_M^2)(V_M - b) = RT$ we express $p = RT/(V_M - b) - a/V_M^2$. The first law $\mathrm{d}U_M = T\,\mathrm{d}S_M - p\,\mathrm{d}V_M$ then gives

$$\left(\frac{\partial U_M}{\partial V_M}\right)_T = T\left(\frac{\partial S_M}{\partial V_M}\right)_T - p = T\left(\frac{\partial p}{\partial T}\right)_{V_M} - p = \frac{a}{V_M^2}$$

and

$$\left(\frac{\partial C_{V,M}}{\partial V_M}\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial U_M}{\partial V_M}\right)_T\right)_{V_M} = 0\,.$$

Thus the heat capacity at constant volume does not depend on volume.

The difference of heat capacities at constant pressure and at constant volume (i.e., density) is equal to

$$C_{p,M} - C_{V,M} = T\left(\frac{\partial p}{\partial T}\right)_{V_M}\left(\frac{\partial V_M}{\partial T}\right)_p = \frac{RT}{V_M - b}\beta V_M\,,$$

where

$$\beta = \frac{1}{V_M}\left(\frac{T}{V_M - b} - \frac{2a}{RV_M^2} + \frac{2ab}{RV_M^3}\right)^{-1}$$

is the volumetric thermal expansion coefficient of the van der Waals gas (Problem 1.5).

The internal energy is given by

$$\begin{aligned} U_M(T, V_M) &= U_M(T', V_M') + \int_{T'}^{T}\left(\frac{\partial U_M}{\partial T}\right)_{V_M}\mathrm{d}T + \int_{V_M'}^{V_M}\left(\frac{\partial U_M}{\partial V_M}\right)_T \mathrm{d}V_M \\ &= U_M(T', V_M') + C_{V,M}(T - T') + a\left(\frac{1}{V_M'} - \frac{1}{V_M}\right). \end{aligned}$$

The equation of a reversible adiabatic process is found by setting

$$\begin{aligned} \mathrm{d}S_M &= \left(\frac{\partial S_M}{\partial T}\right)_{V_M}\mathrm{d}T + \left(\frac{\partial S_M}{\partial V_M}\right)_T \mathrm{d}V_M \\ &= \frac{C_{V,M}}{T}\,\mathrm{d}T + \frac{R}{V_M - b}\,\mathrm{d}V_M = 0\,, \end{aligned}$$

where $(\partial S_M/\partial V_M)_T = (\partial p/\partial T)_{V_M}$. By integrating the thus obtained relation between $\mathrm{d}T$ and $\mathrm{d}V_M$ from $T'$ and $V'_M$ to $T$ and $V_M$ one finds that the adiabat reads

$$C_{V,M} \ln \frac{T}{T'} = R \ln \frac{V'_M - b}{V_M - b} \,.$$

**Problem 4.7.**
*Calculate the amount of heat exchanged by* 1 kg *of saturated water vapor with its environment when heated from* 100 °C *to* 101 °C*! During the process, pressure is adjusted as needed so as to keep the vapor saturated at all times; the heat capacity at constant pressure is equal to* 1890 J/kgK.

The heat exchanged upon a reversible infinitesimal change of temperature and pressure is given by

$$\mathrm{d}Q = T\,\mathrm{d}S = T\left[\left(\frac{\partial S}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial S}{\partial p}\right)_T \mathrm{d}p\right].$$

The first term can be expressed in terms of heat capacity at constant pressure, $T(\partial S/\partial T)_p = mc_p$, whereas the second one depends on the thermal expansion coefficient as seen from the appropriate Maxwell relation: $T(\partial S/\partial p)_T = -T(\partial V/\partial T)_p = -\beta T V$. We describe vapor as an ideal gas so that $\beta T V = mRT/pM$. Thus

$$Q = m\left[c_p - \frac{RT}{pM}\left(\frac{\partial p}{\partial T}\right)_\mu\right]\Delta T \,.$$

Here the subscript $\mu$ emphasizes the derivative is to be evaluated under the constraint of equal chemical potentials of liquid water and vapor, which are in equilibrium. The derivative can be calculated from the Clausius–Clapeyron equation or obtained from the steam table (see Appendix A): $(\partial p/\partial T)_\mu \approx 3900$ Pa/K. Finally, we find that $Q = -4830$ J, indicating that heat is emitted by the saturated vapor. This happens because the heat emitted by vapor due to the increase of pressure exceeds the heat needed to increase the temperature.

**Problem 4.8.**
*The surface area of a soap film with a heat capacity of* 0.01 J/K *is increased by* $0.2\ \mathrm{m}^2$*. How much heat is exchanged with the environment if the expansion of the film is isothermal at* 278 K, *and how much work is expended in the process? The temperature dependence of the surface tension is given by*

$$\gamma(T) = \gamma_0\left(\frac{T_c - T}{T_c - T_0}\right)^n ,$$

*where* $n = 1.2$, $\gamma_0 = 0.03$ N/m, $T_0 = 273$ K, and $T_c = 647$ K. *What is the temperature change if the expansion is adiabatic? What is the dependence of the heat capacity at constant surface area on film area?*

The pairs of variables of interest are temperature and entropy ($T$ and $S$) and surface tension and area ($\gamma$ and $A$). The heat associated with isothermal expansion by $\Delta A$ reads $Q = T_1 \Delta S$, where at $T_1 = 278$ K and the change of entropy $\Delta S \approx (\partial S/\partial A)_T\, \Delta A$. Using the Maxwell relation $(\partial S/\partial A)_T = -(\partial\gamma/\partial T)_A$ and the above functional form of $\gamma(T)$, one has

$$Q \approx T_1 \gamma_0 n \frac{(T_c - T_1)^{n-1}}{(T_c - T_0)^n}\, \Delta A = 5.3\ \mathrm{mJ}\,.$$

Heat is absorbed by the soap film. At the same time, the work supplied to the film equals

$$W = \gamma(T_1)\Delta A = 5.9\ \mathrm{mJ}\,.$$

To calculate the change of temperature upon reversible adiabatic expansion we start with the differential form of the adiabat: $\mathrm{d}S = (\partial S/\partial T)_A\, \mathrm{d}T + (\partial S/\partial A)_T\, \mathrm{d}A = 0$. The first term involves the heat capacity at constant film area $C_A$ and the second one can be recast using the above Maxwell relation. We find that

$$\begin{aligned}\left(\frac{\partial T}{\partial A}\right)_S &= -\left(\frac{\partial S}{\partial A}\right)_T \Big/ \left(\frac{\partial S}{\partial T}\right)_A = \left(\frac{\partial \gamma}{\partial T}\right)_A \frac{T}{C_A}\\ &= -\frac{\gamma_0 n}{C_A} \frac{T(T_c - T)^{n-1}}{(T_c - T_0)^n}\,.\end{aligned}$$

If we assume that $C_A = const.$ then

$$\Delta T \approx \left(\frac{\partial T}{\partial A}\right)_S \Delta A = -0.53\ \mathrm{K}\,.$$

In order to find the dependence of $C_A$ on film area $A$ we first calculate the derivative

$$\begin{aligned}\left(\frac{\partial C_A}{\partial A}\right)_T &= T\left(\frac{\partial}{\partial A}\left(\frac{\partial S}{\partial T}\right)_A\right)_T = T\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial A}\right)_T\right)_A\\ &= -T\left(\frac{\partial^2 \gamma}{\partial T^2}\right)_A = -T\gamma_0 n(n-1)\frac{(T_c - T)^{n-2}}{(T_c - T_0)^n}\,.\end{aligned}$$

This gives

$$\Delta C_A \approx \left(\frac{\partial C_A}{\partial A}\right)_T \Delta A = 1.9 \times 10^{-6}\ \mathrm{J/K} \ll C_A\,,$$

which justifies the above assumption of constant $C_A$ in the adiabatic process.

**Problem 4.9.**
*The isothermal Young modulus of steel at* $20\,^\circ\mathrm{C}$ *is equal to* $2 \times 10^{11}\ \mathrm{N/m^2}$. *Find the value of the corresponding adiabatic modulus at this temperature! The linear thermal expansion coefficient of steel is* $10.6 \times 10^{-6}\ \mathrm{K^{-1}}$, *its heat capacity at constant pressure is* $500\ \mathrm{J/kgK}$, *and its density is* $7800\ \mathrm{kg/m^3}$.

As the Young modulus is defined based on uniaxial deformation of a rod, the pairs of thermodynamic variables are the length of the steel rod and external stretching force ($\ell$ and $\mathcal{F}$) and temperature and entropy ($T$ and $S$). We look for the relation between the isothermal and adiabatic Young modulus $E_T = (\ell/A)(\partial\mathcal{F}/\partial\ell)_T$ and $E_S = (\ell/A)(\partial\mathcal{F}/\partial\ell)_S$, respectively, where $A$ denotes the cross section of the rod. To this end, we spell out the total differential of entropy seen as a function of $T$ and $\mathcal{F}$

$$\mathrm{d}S = \frac{mc_{\mathcal{F}}}{T}\,\mathrm{d}T + \left(\frac{\partial\ell}{\partial T}\right)_{\mathcal{F}}\mathrm{d}\mathcal{F}$$

and $T$ and $\ell$

$$\mathrm{d}S = \frac{mc_{\ell}}{T}\,\mathrm{d}T - \left(\frac{\partial\mathcal{F}}{\partial T}\right)_{\ell}\mathrm{d}\ell$$

[where we used the Maxwell relations $(\partial S/\partial\mathcal{F})_T = (\partial\ell/\partial T)_{\mathcal{F}}$ and $(\partial S/\partial\ell)_T = -(\partial\mathcal{F}/\partial T)_\ell$] and set them to 0. By combining the thus obtained adiabats we find that $(\partial\mathcal{F}/\partial\ell)_S = (c_{\mathcal{F}}/c_\ell)(\partial\mathcal{F}/\partial\ell)_T$, which gives

$$E_S = \frac{c_{\mathcal{F}}}{c_\ell}E_T\,.$$

The difference of heat capacities $c_{\mathcal{F}} - c_\ell$ is calculated just like in Problem 4.2:

$$c_{\mathcal{F}} - c_\ell = T\left(\frac{\partial\mathcal{F}}{\partial\ell}\right)_T\left(\frac{\partial\ell}{\partial T}\right)_{\mathcal{F}}^2 = \frac{T\alpha^2E_T}{\rho} = 0.84\ \mathrm{J/kgK}\,,$$

where $\alpha$ is the linear thermal expansion coefficient of steel and $\rho$ is the density. By assuming that $c_{\mathcal{F}} \approx c_p = 500$ J/kgK, we find that $E_S/E_T = 1.0017$ and $E_S = 2.0034 \times 10^{11}\ \mathrm{N/m^2}$.

If one were more careful one should also consider the dependence of $c_{\mathcal{F}}$ on the force $\mathcal{F}$. Like in Problem 4.8 we write

$$\left(\frac{\partial c_{\mathcal{F}}}{\partial\mathcal{F}}\right)_T = \frac{T}{m}\left(\frac{\partial^2\ell}{\partial T^2}\right)_{\mathcal{F}} = \frac{T\alpha^2}{\rho A}$$

so that $c_{\mathcal{F}}(\mathcal{F}) = c_{\mathcal{F}}(0) + T\alpha^2\mathcal{F}/\rho A$. The relative correction to $c_{\mathcal{F}} - c_\ell$ is equal to $\mathcal{F}/AE_T$ and is negligible for small $\mathcal{F}$.

## Problem 4.10.

*The internal energy of a non-ideal gas is given by* $U(T, V) = C_V T - a/V$, *where* $C_V = 0.83$ J/K *and* $a = 0.01$ Jm$^3$. *The gas fills a sealed one-liter vessel at* 1 bar *and* 27 °C. *How much heat must be supplied to achieve a pressure increase of* 10%*? What is the final temperature and by how much does the entropy change?*

We first calculate the final temperature. From the differential $\mathrm{d}U = C_V\,\mathrm{d}T + (a/V^2)\,\mathrm{d}V$ we see that $(\partial U/\partial V)_T = a/V^2$. At the same time, $\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V$ gives

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p = \frac{a}{V^2},$$

where we used the Maxwell relation $(\partial S/\partial V)_T = (\partial p/\partial T)_V$. We recognize that $T(\partial p/\partial T)_V - p = T^2\big(\partial(p/T)/\partial T\big)_V$ and integrate the above equation, after separating the variables, at constant volume from the initial state at temperature $T'$ and pressure $p'$ to the final state at temperature $T$ and pressure $p$. The final temperature is

$$T = T'\frac{p + a/V^2}{p' + a/V^2} = 54.3\,^\circ\mathrm{C}.$$

As the temperature increase occurs at constant volume, the heat supplied to the system is equal to the change of the internal energy: $Q = \Delta U = C_V(T - T') = 22.7$ J. The change of entropy is

$$\Delta S = \int_{T'}^{T} \frac{C_V}{T}\,\mathrm{d}T = C_V \ln\left(\frac{T}{T'}\right) = 0.072\ \mathrm{J/K}.$$

## Problem 4.11.

*Consider a one-liter sample of cold plasma at* 2000 K *containing* $5 \times 10^{14}$ *atoms. Calculate the relative deviation of the difference of heat capacities* $c_p - c_V$ *from the ideal-gas result! The pressure of plasma is given by*

$$p = nk_BT - \frac{an^{3/2}}{3T^{1/2}},$$

*where* $a = 5.5 \times 10^{-29}$ Jm$^{3/2}$K$^{1/2}$ *and* $n$ *denotes the number density of atoms.*

To evaluate $c_p - c_V = T\beta^2/\rho\chi_T$ we need the volumetric thermal expansion coefficient $\beta$ and the isothermal compressibility $\chi_T$ of plasma. $\beta$ can be obtained by an implicit differentiation of the equation of state $p = p(T, V)$ with respect to temperature at constant pressure. To the lowest order we have

$$\beta T = \frac{T}{V}\left(\frac{\partial V}{\partial T}\right)_p = 1 + \frac{2b}{3},$$

where $b = an^{1/2}/k_BT^{3/2} \ll 1$. Similarly, we find that the isothermal compressibility is

$$\chi_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \frac{V}{Nk_BT}\left(1+\frac{b}{2}\right),$$

so that

$$c_p - c_V = \frac{R}{M}\left(1+\frac{5b}{6}\right),$$

where $R = N_Ak_B$. The relative correction to $c_p - c_V$ is $5b/6$, which amounts to 2.6%.

**Problem 4.12.**

*At* 300 K, *the magnetic susceptibility of an ideal gas is equal to* $4 \times 10^{-7}$. *At this temperature and a pressure of* 1 bar, 10 l *of this gas is exposed to a magnetic field of strength of* $10^6$ A/m. *Determine the relative change of the volume of the gas due to the magnetic field if both pressure and temperature are kept constant! How much heat does the gas exchange with the environment? The pressure and temperature derivatives of the susceptibility* $\chi$ *are equal to* $(\partial\chi/\partial p)_T = 10^{-12}\ \mathrm{Pa}^{-1}$ *and* $(\partial\chi/\partial T)_p = -10^{-9}\ \mathrm{K}^{-1}$, *respectively.*

The three pairs of conjugate thermodynamic variables of interest are temperature and entropy ($T$ and $S$), pressure and volume ($p$ and $V$), magnetic field strength and magnetic moment ($H$ and $MV$). The first law reads $\mathrm{d}U = T\,\mathrm{d}S + \mu_0 H\,\mathrm{d}(MV) - p\,\mathrm{d}V$ and we need to calculate

$$\left(\frac{\partial V}{\partial H}\right)_{T,p} = -\mu_0\left(\frac{\partial(MV)}{\partial p}\right)_{T,H} = \mu_0 VH\left[\chi_T\chi - \left(\frac{\partial\chi}{\partial p}\right)_T\right],$$

where $\chi = M/H$ is the magnetic susceptibility and $\chi_T = 1/p$ is the isothermal compressibility. Upon integration, we find that $\Delta V/V \approx 1.9 \times 10^{-6}$.

The heat exchanged by the gas with the environment is equal to

$$\begin{aligned} Q &= T\int_0^H \left(\frac{\partial S}{\partial H}\right)_{T,p}\mathrm{d}H = T\mu_0\int_0^H\left(\frac{\partial(MV)}{\partial T}\right)_{p,H}\mathrm{d}H \\ &= \frac{1}{2}\mu_0 VH^2\left[\chi\beta + \left(\frac{\partial\chi}{\partial T}\right)_p\right]. \end{aligned}$$

As $\beta = 1/T$, we finally have $Q = 6.3 \times 10^{-4}$ J.

**Problem 4.13.**

*A one-liter vessel is filled with water containing dissolved paramagnetic ions and then sealed so as to keep the volume constant. Find the change of pressure in the vessel after it is exposed to a magnetic field of strength* $1.6 \times 10^7$ A/m *at a constant temperature of* 20 °C*! By how much do the pressure and temperature change if the vessel is* *thermally insulated? The magnetization of the ion solution is given by* $M(H, T, V) = aH/TV$ *with* $a = 10^{-7}$ $\mathrm{m^3K}$. *The density of the solution is* $10^3$ $\mathrm{kg/m^3}$, *its heat capacity in absence of magnetic field is* 4190 J/kgK, *the compressibility is* $0.46 \times 10^{-9}$ $\mathrm{Pa^{-1}}$, *and the thermal expansion coefficient is* $2.1 \times 10^{-4}$ $\mathrm{K^{-1}}$.

As in Problem 4.2 one has $\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu_0 H\,\mathrm{d}(MV)$. The derivative $(\partial p/\partial H)_{T,V}$ is obtained using a suitable Maxwell relation, starting from the equation of state $M = M(H, T, V)$:

$$\left(\frac{\partial p}{\partial H}\right)_{T,V} = \mu_0 \left(\frac{\partial (MV)}{\partial V}\right)_{T,H} = 0\,.$$

There is no change of pressure in the isothermal experiment.

When considering the thermally insulated vessel, one first observes that the internal energy does not depend on the field strength $H$:

$$\left(\frac{\partial U}{\partial H}\right)_{T,V} = T\left(\frac{\partial S}{\partial H}\right)_{T,V} + \mu_0 H\left(\frac{\partial (MV)}{\partial H}\right)_{T,V} = 0\,,$$

and hence $U = U(T, V)$; here we took into account that $(\partial S/\partial H)_{TV} = \mu_0\big(\partial(MV)/\partial T\big)_{H,V}$ and the specific form of $M = M(H, T, V)$. Since in an isochoric adiabatic process both heat exchanged and mechanical work done vanish, it follows that $\mathrm{d}U = \mu_0 H\,\mathrm{d}(MV)$ and $\mathrm{d}U = (\partial U/\partial T)_{H,V}\,\mathrm{d}T = mc_V\,\mathrm{d}T$, where $c_V$ stands for the heat capacity of the solution in absence of magnetic field. By spelling out $\mathrm{d}(MV)$, one arrives at the adiabatic equation in the differential form

$$\left(mc_V + \frac{\mu_0 a H^2}{T^2}\right)\mathrm{d}T = \frac{\mu_0 a}{T} H\,\mathrm{d}H\,.$$

The second term in the bracket on the left-hand side is just a minor correction to the heat capacity and is neglected. The final temperature is obtained by integration:

$$T = \sqrt{T'^2 + \frac{\mu_0 a H^2}{\rho V c_V}}\,,$$

where $T'$ and $\rho$ denote the initial temperature and the density of the solution, respectively. The temperature increase is rather small, amounting to $\Delta T = T - T' = 1.3 \times 10^{-5}$ K. Finally, from the equation of isochore $\mathrm{d}V = \beta V\,\mathrm{d}T - V\chi_T\,\mathrm{d}p + (\partial V/\partial H)_{T,p}\mathrm{d}H = 0$ [here $\chi_T$ is the isothermal compressibility and $\beta$ is the thermal expansion coefficient, whereas $(\partial V/\partial H)_{T,p} = 0$ for the equation of state in question] one concludes that $(\partial p/\partial T)_V = \beta/\chi_T$ and

$$\Delta p = \frac{\beta}{\chi_T}\,\Delta T \approx 6\ \mathrm{Pa}\,.$$

## Problem 4.14.

$10\ \mathrm{cm}^3$ *of a liquid at* $20\,^\circ\mathrm{C}$ *is compressed isothermally so that the volume decreases by* $0.1\%$. *During the process*, $3\ \mathrm{J}$ *of heat is emitted. How would the temperature change if compression were adiabatic and reversible, with the same volume change and initial temperature as in the isothermal case? The density of the liquid prior to compression is equal to* $0.85\ \mathrm{kg/dm}^3$ *and its heat capacity at constant volume is* $2.8\ \mathrm{kJ/kgK}$. *Assume that the compression does not affect the heat capacity, isothermal compressibility, and the thermal expansion coefficient of the liquid.*

The heat emitted by the liquid upon isothermal compression at $T'$ is

$$Q = T' \int_{V'}^{V} \left(\frac{\partial S}{\partial V}\right)_T \mathrm{d}V = T' \int_{V'}^{V} \frac{\beta}{\chi_T}\,\mathrm{d}V = \frac{\beta T'}{\chi_T}(V - V')\,;$$

$\beta$ and $\chi_T$ denote the thermal expansion coefficient and the isothermal compressibility, respectively. Upon adiabatic compression we have

$$\mathrm{d}S = \left(\frac{\partial S}{\partial V}\right)_T \mathrm{d}V + \left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T = \frac{\beta}{\chi_T}\,\mathrm{d}V + \frac{mc_V}{T}\,\mathrm{d}T = 0\,.$$

After integrating from $T'$ to $T$ and from $V'$ to $V$ we find that the final temperature is given by

$$T = T' \exp\left(-\frac{Q}{mc_V T'}\right)$$

and $T - T' = 0.126\ \mathrm{K}$.

## Problem 4.15.

*Calculate the pressure in a water droplet of radius of* $10\ \mu\mathrm{m}$ *if it carries an electric charge equivalent to* $1000$ *electrons! At what radius is the pressure largest? At what relative humidity does the droplet at* $20\,^\circ\mathrm{C}$ *start to grow? At* $20\,^\circ\mathrm{C}$, *the surface tension of water is equal to* $0.073\ \mathrm{N/m}$ *and the saturated vapor pressure is* $2337\ \mathrm{Pa}$.

According to the Laplace law, the pressure in an uncharged droplet of radius $r$ exceeds the ambient pressure by $p_\gamma = 2\gamma/r$; here $\gamma$ is the surface tension. In a droplet carrying an electric charge $e$, repulsion between the evenly distributed charge gives rise to an additional electrostatic pressure $p_e$ which can be derived from the principle of virtual work where the volume of the droplet is infinitesimally increased by $\mathrm{d}V$ and one calculates the electrostatic work $\mathrm{d}W$ needed for this. We have $p_e = \mathrm{d}W/\mathrm{d}V = \Delta w$: The correction to the pressure is equal to the change of density of the electrostatic energy $w = ED/2$. From the Gauss law one finds that the strength of the electric field inside the droplet is $E = 0$, whereas outside at the droplet surface it is $E = e/4\pi\epsilon_0 r^2$. The difference between the pressure inside the droplet and the outside pressure is then

$$\Delta p = p_\gamma + p_e = \frac{2\gamma}{r} + \Delta w = \frac{2\gamma}{r} - \frac{e^2}{32\pi^2\epsilon_0 r^4}\,.$$

In droplets of diameter of 10 $\mu$m we obtain $\Delta p \approx 1.46 \times 10^4$ Pa so that the electrostatic contribution can be neglected. By plotting $\Delta p = \Delta p(r)$ (Fig. 4.2), we see that the pressure difference exhibits a maximum at $r_{\max} = \sqrt[3]{e^2/16\pi^2\epsilon_0\gamma} \approx 63$ nm.

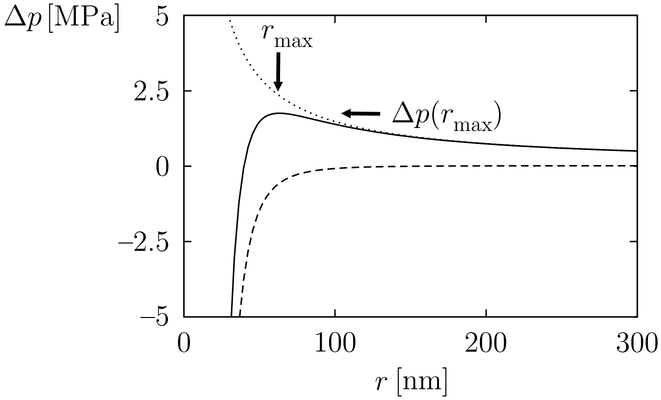

**Fig. 4.2** Pressure inside a charged water droplet (solid line) as a function of its radius: The electrostatic pressure (dashed line) is negative, whereas the Laplace pressure (dotted line) is positive

In order to establish the relation between the pressure change $\Delta p$ inside the droplet and the humidity of ambient air, we must consider both mechanical equilibrium and chemical equilibrium. In the latter, the chemical potentials of liquid water in droplets $\mu_l$ and of water vapor in the atmosphere $\mu_v$ must be equal:

$$\mu_l(T, p_0 + p_r + \Delta p) = \mu_v(T, p_r)\,.$$

Here $p_0$ is the partial pressure of dry air and $p_r$ is the partial pressure of vapor in equilibrium with droplets of diameter $r$. At a given temperature, liquid water under a flat surface ($r \to \infty$) is in equilibrium with vapor at a saturated vapor pressure $p_\infty$ or

$$\mu_l(T, p_0 + p_\infty) = \mu_v(T, p_\infty)\,.$$

For $p_r - p_\infty + \Delta p \ll p_0 + p_\infty$ we have

$$\mu_l(T, p_0 + p_r + \Delta p) = \mu_l(T, p_0 + p_\infty) + \frac{p_r - p_\infty + \Delta p}{\rho_l}\,,$$

where $\rho_l$ is the density of water. As vapor can be treated as an ideal gas of kilomolar mass $M$,

$$\mu_v(T, p_r) = \mu_v(T, p_\infty) + \frac{RT}{M}\ln\frac{p_r}{p_\infty}\,.$$

Now we combine these expressions, expand $\ln(p_r/p_\infty) \approx p_r/p_\infty - 1$ for $p_r \approx p_\infty$, and express $p_r$:

$$p_r = p_\infty + \frac{\rho_v}{\rho_l}\,\Delta p\,.$$

Here $\rho_v \approx p_\infty M/RT$; we took into account that $\rho_l \gg \rho_v$.

If $\Delta p$ is much smaller than the atmospheric pressure (i.e., in large enough droplets), the same result is obtained from the chemical equilibrium alone. Because the ratio of water and vapor densities $\rho_l/\rho_v$ is large, the mechanical equilibrium is then only slightly violated.

For 10 $\mu$m droplets that carry 1000 elementary charges, we obtain $p_r \approx 2337.25$ Pa; here we used $\rho_l$ and $\rho_v$ from the steam table (Appendix A). At 20 °C, these droplets are in equilibrium with air of relative humidity of

$$\eta = \frac{p_r}{p_\infty} = 100.01\,\%\,.$$

If the humidity is larger than this, the 10 $\mu$m droplets begin to grow since the chemical potential of water vapor exceeds the chemical potential of water in them. If the vapor pressure is raised above $p_r(r_{\max}) \approx 30.1$ Pa, which at 20 °C corresponds to a relative humidity of 101.3 %, droplets of all sizes grow. (The last result was obtained by assuming that the above approximations are justified, which may not necessarily be the case.)

**Problem 4.16.**

*A vessel contains liquid water and vapor at* 100 °C. *Calculate the change of the partial pressure of vapor after the vessel is filled with an inert gas of a partial pressure of* 20 bar. *The inert gas does not dissolve in water. The dependence of the density of water on pressure is given by*

$$\rho_l(p) = \rho_0\left[1 + \chi_T(p - p_s')\right],$$

*where* $\rho_0 = 959\ \mathrm{kg/m^3}$ *and* $\chi_T = 0.46 \times 10^{-9}\ \mathrm{Pa^{-1}}$ *are the density and the isothermal compressibility of water at* 100 °C, *respectively, whereas* $p_s' = 1.01$ bar *is the saturated vapor pressure at this temperature.*

In the reference state, the chemical potentials of liquid water and vapor are equal: $\mu_l(p_s', T) = \mu_v(p_s', T)$. After the atmospheric pressure is increased, the chemical potential of water is increased by $\Delta\mu_l = \int_{p_s'}^{p_s+p} \rho_l^{-1}(p)\,\mathrm{d}p$, where $p_s$ denotes the new saturated vapor pressure and $p$ is the pressure of the inert gas. The change in the chemical potential of water vapor is $\Delta\mu_v = (RT/M)\ln\left(p_s/p_s'\right)$. In equilibrium one has $\mu_l(p_s + p, T) = \mu_v(p_s, T)$ and after calculating $\Delta\mu_l$ for the above $\rho_l(p)$, we have

$$\frac{1}{\rho_0\chi_T}\ln\Big(1 + \chi_T\left(p_s + p - p_s'\right)\Big) = \frac{RT}{M}\ln\frac{p_s}{p_s'}\,.$$

This equation can be solved approximately by assuming that the change of vapor pressure is small compared to the pressure of the inert gas, i.e., $p_s - p'_s \ll p$. Then

$$p_s = p'_s\,(1 + \chi_T p)^{M/RT\rho_0\chi_T} = 1.022\ \mathrm{bar}\,.$$

**Problem 4.17.**
*Assume that the equation of state for solid iron is given by*

$$V = \frac{m}{\rho}\,(1 + \beta T - \chi_T p)$$

*and that its heat capacity is given by*

$$c_V = \frac{3R}{M}\frac{T^3}{T_D^3 + T^3}\,.$$

*Derive the equation of reversible adiabatic process! Calculate the stress generated in an initially unconstrained thermally insulated sample after it is isotropically compressed, which gives rise to an increase of temperature from* 300 to 310 K*! Here* $\rho = 7800\ \mathrm{kg/m^3}$ *is the density of iron,* $\beta = 3\times10^{-5}\ \mathrm{K^{-1}}$ *is the thermal expansion coefficient,* $\chi_T = 3.6\times10^{-12}\ \mathrm{Pa^{-1}}$ *is the isothermal compressibility,* $M = 55.5\ \mathrm{kg/kmol}$ *is the kilomolar mass, and* $T_D = 470\ \mathrm{K}$ *is the Debye temperature.*

We start with the total differential of entropy which reads $\mathrm{d}S = (\partial S/\partial T)_V\,\mathrm{d}T + (\partial S/\partial V)_T\,\mathrm{d}V = (mc_V/T)\,\mathrm{d}T + (\beta/\chi_T)\,\mathrm{d}V$. With the above form of $c_V$ and constant $\beta$ and $\chi_T$, $\mathrm{d}S$ can be integrated to obtain a closed expression for entropy $S(T,V) = (mR/M)\ln\bigl(1 + (T/T_D)^3\bigr) + (\beta/\chi_T)(V - V_0)$, where $V_0 = V(T = 0, p = 0)$. After inserting the equation of state and dividing by $m$, we have

$$s(T,p) = \frac{R}{M}\ln\left(1 + \left(\frac{T}{T_D}\right)^3\right) + \frac{\beta^2}{\rho\chi_T}T - \frac{\beta}{\rho}p$$

so that an adiabatic process in solid iron is described by

$$p_2 = p_1 + \frac{\rho R}{\beta M}\ln\frac{1 + (T_2/T_D)^3}{1 + (T_1/T_D)^3} + \frac{\beta}{\chi_T}(T_2 - T_1)\,.$$

The stress in the adiabatically compressed sample is $9\times10^8$ Pa.

**Problem 4.18.**
*Calculate the isothermal and adiabatic compressibility of black-body radiation at* 20 °C*! Recall that for radiation* $p = u/3$ *and* $u = 4\sigma T^4/c$*, where* $p$ *is the pressure,*

*u is the volumetric density of internal energy, $\sigma$ is the Stefan constant, and c is the speed of light in vacuum.*

Since the radiation pressure depends solely on temperature, it remains constant during an isothermal volume change; therefore, the isothermal compressibility of radiation is infinite.

Adiabatic compressibility, on the other hand, is obtained from $\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V$ which gives

$$\mathrm{d}S = \frac{16\sigma T^3}{3c}\,\mathrm{d}V + \frac{16\sigma T^2 V}{c}\,\mathrm{d}T\,.$$

We set $\mathrm{d}S = 0$ to find that $\mathrm{d}V/V = -3\,\mathrm{d}T/T$. From the equation of state we have $\mathrm{d}p/p = 4\,\mathrm{d}T/T$, which leads to $\mathrm{d}V/V = -\left(9c/16\sigma T^4\right)\mathrm{d}p$ and

$$\chi_S = \frac{9c}{16\sigma T^4}\,.$$

At room temperature, $\chi_S = 4.04 \times 10^5\ \mathrm{Pa}^{-1}$.

**Problem 4.19.**
*Derive the adiabatic equation for black-body radiation! What was the density of the universe at a time when the temperature of the cosmic background radiation was* 3000 K *relative to the present value which corresponds to a temperature of* 3 K*?*

Problem 4.18 shows that in an adiabatic process for black-body radiation $\mathrm{d}V/V = -3\,\mathrm{d}T/T$ so that

$$TV^{1/3} = const.$$

By taking into account that $p \propto T^4$, this result can be recast as

$$pV^{4/3} = const.$$

The first relation gives $V'/V = \rho/\rho' = \left(T/T'\right)^3$ which implies that at the time when the temperature of radiation was 3000 K, the density of the universe was $10^9$-times larger than today.

**Problem 4.20.**
*What is the highest pressure at which nitrogen is cooled upon Joule–Kelvin expansion? What is the volume at the extreme inversion point? Assume that nitrogen can be described by the second Dieterici equation of state*

$$\left(p + \frac{a}{V_M^{5/3}}\right)(V_M - b) = RT$$

*and first rewrite it in a dimensionless form! The critical parameters for nitrogen are* $p_c = 34.5$ bar, $V_{Mc} = 89.6$ l/kmol, *and* $T_c = 125.9$ K.

In the critical point $(\partial p/\partial V_M)_T = \left(\partial^2 p/\partial V_M^2\right)_T = 0$. These conditions, together with the equation of state, result in the following system of equations: $pV_M - pb + a/V_M^{2/3} - ab/V_M^{5/3} = RT, p - 2a/3V_M^{5/3} + 5ab/3V_M^{8/3} = 0$, and $10a/3V_M^{8/3} - 40ab/3V_M^{11/3} = 0$, from where we extract $V_{Mc} = 4b$, $p_c = a/4^{8/3}b^{5/3}$, and $T_c = 15a/4^{8/3}Rb^{2/3}$. By introducing reduced variables $\mathcal{P} = p/p_c$, $\mathcal{V} = V_M/V_{Mc}$, and $\mathcal{T} = T/T_c$, we rewrite the equation of state in the dimensionless form:

$$\left(\mathcal{P} + \frac{4}{\mathcal{V}^{5/3}}\right)(4\mathcal{V} - 1) = 15\mathcal{T}\,.$$

The Joule–Kelvin coefficient $(\partial T/\partial p)_H = (\beta T - 1)/\rho c_p$ vanishes for $\beta = 1/T$, i.e., for

$$\left(\frac{\partial \mathcal{V}}{\partial \mathcal{T}}\right)_{\mathcal{P}} = \frac{\mathcal{V}}{\mathcal{T}}\,.$$

This derivative is obtained by differentiating the equation of state: $-20(4\mathcal{V} - 1)/3\mathcal{V}^{8/3} + 4\left(\mathcal{P} + 4/\mathcal{V}^{5/3}\right) = 15\,(\partial\mathcal{T}/\partial\mathcal{V})_{\mathcal{P}}$. From here we calculate the inversion temperature $\mathcal{T}_i = 4\,(4\mathcal{V} - 1)^2\,/9\mathcal{V}^{5/3}$ and the inversion curve

$$\mathcal{P}_i = \frac{16}{3\mathcal{V}^{2/3}}\left(5 - \frac{2}{\mathcal{V}}\right).$$

The inversion curve plotted in Fig. 4.3 is negative for $\mathcal{V} < 2/5$, whereas for large $\mathcal{V}$ it decreases as $80/3\mathcal{V}^{2/3}$. Evidently, it has an extreme in between these

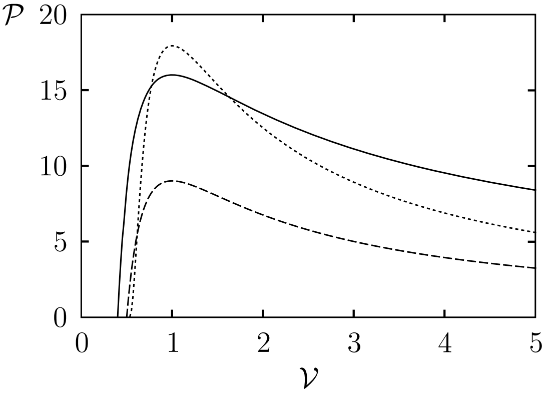

**Fig. 4.3** Inversion curve for the second Dieterici equation of state (solid line) as well as for the first Dieterici (dotted line) and the van der Waals equation of state (dashed line)

two regimes; the extreme is located at $\mathcal{V} = 1$ which gives $\mathcal{P}_i = 16$ and $\mathcal{T}_i = 4$. The extreme inversion point hence corresponds to a pressure of $16 p_c = 552$ bar, the kilomolar volume of $V_{Mc} = 89.6$ l/kmol, and a temperature of $4T_c = 504$ K.

A similar analysis can be done for the first Dieterici equation. In this case, the inversion curve in $\mathcal{PV}$ plane reads

$$\mathcal{P}_i = \frac{4}{\mathcal{V}} \exp\left(2 - \frac{1}{4\mathcal{V} - 2}\right)$$

with $\mathcal{T}_i = 8 - 4/\mathcal{V}$. The extreme inversion point is located at a pressure of $4\exp(3/2)p_c = 17.93\, p_c$, a kilomolar volume of $V_{Mc}$, and a temperature of $4T_c$. The corresponding results for the van der Waals gas are

$$\mathcal{P}_i = \frac{9}{\mathcal{V}}\left(2 - \frac{1}{\mathcal{V}}\right)$$

and $\mathcal{T}_i = 3\,(3 - 1/\mathcal{V})^2\,/4$. Here the extreme inversion point is found at a pressure of $9p_c$, and a kilomolar volume of $V_{Mc}$, and a temperature of $3T_c$.

**Problem 4.21.**
*At what temperature does the Joule–Kelvin coefficient of water vapor change sign if vapor is described by the Callendar equation of state*

$$V_M - b = \frac{RT}{p} - \frac{a}{T^{10/3}}\,,$$

*where $V_M$ denotes the kilomolar volume,* $b = 0.03\ \mathrm{m^3/kmol}$, *and* $a = 6.8 \times 10^6\ \mathrm{m^3\, K^{10/3}/kmol}$*?*

The Joule–Kelvin coefficient is $(\partial T/\partial p)_H = (\beta T - 1)/\rho c_p$ (Problem 4.4) and changes sign when $\beta T - 1 = RT/pV_M + 10a/3V_M T^{10/3} - 1 = 0$. Thus the inversion temperature is equal to

$$T_i = \left(\frac{13a}{3b}\right)^{3/10} = 498\ \mathrm{K}\,.$$

**Problem 4.22.**
*A sealed vessel contains* 0.1 l *of rarefied gas consisting of polar molecules. Each molecule carries an electric dipole moment of* $2 \times 10^{-27}$ Asm. *How much work is expended at* 20 °C *as the electric field strength is increased from* $10^7$ V/m *to* $10^8$ V/m*? How much heat is exchanged in the process? The pressure of the gas is* 1 mbar *and its polarization is given by*

$$P = np_e\left(\coth\frac{p_e E}{k_B T} - \frac{k_B T}{p_e E}\right),$$

*where n is the number density of the molecules,* $p_e$ *is the electric dipole moment, and E is the electric field strength.*

As the process takes place at constant volume, the first law $\mathrm{d}U = T\,\mathrm{d}S + E\,\mathrm{d}(VP) - p\,\mathrm{d}V$ includes only heat and electrical work. The electrical work is

$$W = \int_{E_1}^{E_2} EV\,\mathrm{d}P = V\int_{E_1}^{E_2} E\left(\frac{\partial P}{\partial E}\right)_{T,V}\mathrm{d}E\,,$$

where we took into account that the volume does not depend on the electric field strength, which can be deduced from the total differential of the Gibbs free energy $\mathrm{d}G' = -S\,\mathrm{d}T - VP\,\mathrm{d}E + V\,\mathrm{d}p$. This gives $(\partial V/\partial E)_{T,p} = -\big(\partial(VP)/\partial p\big)_{T,E}$: The right-hand side is the derivative of the dipole moment of the gas with respect to pressure and is equal to 0. At the given $p_e$, $E$, and $T$, we can replace the equation of state $P(E,T)$ by its low-temperature approximation $np_e\,(1 - k_BT/p_eE)$; as the gas is rarefied, we also use $p = nk_BT$. Thus we obtain

$$W = nk_BTV\int_{E_1}^{E_2}\frac{\mathrm{d}E}{E} = pV\ln\frac{E_2}{E_1} = 23\ \mathrm{mJ}\,.$$

The heat exchanged is given by

$$Q = \int_{E_1}^{E_2} T\,\mathrm{d}S = T\int_{E_1}^{E_2}\left(\frac{\partial S}{\partial E}\right)_{T,V}\mathrm{d}E\,,$$

where the derivative $(\partial S/\partial E)_{T,V} = \big(\partial(VP)/\partial T\big)_{E,V}$ follows from the differential $\mathrm{d}G'' = -S\,\mathrm{d}T - VP\,\mathrm{d}E - p\,\mathrm{d}V$. For the above equation of state where $P = P(E/T)$, $(\partial P/\partial E)_{T,V} = -(T/E)\,(\partial P/\partial T)_{E,V}$ so that the heat exchanged is exactly equal but opposite to the work expended: $Q = -W = -23$ mJ. Thus the internal energy remains unchanged.

**Problem 4.23.**
*A bakelite cuboid is placed in a plate capacitor, filling exactly all its volume. The cuboid is pulled from its initial position such that only half of it remains in the capacitor and released. Find the frequency of oscillations of the cuboid! The plates measure* 5 cm × 20 cm *and are* 1 cm *apart, the voltage between them is* 3000 V, *the relative permittivity of bakelite is* 4, *and its density is* 1200 kg/m$^3$. *Assume that friction is negligible and disregard any effects related to the finite size of the capacitor.*

We first identify the appropriate thermodynamic potential. The differential of the Helmholtz free energy of the cuboid is given by $\mathrm{d}F = -S\,\mathrm{d}T + E\,\mathrm{d}(VP)$ and since polarization is proportional to the strength of the electric field, $P = (\epsilon - 1)\epsilon_0 E$, we have

$$F(T,E) = F(T,0) + \frac{V}{2}(\epsilon - 1)\epsilon_0 E^2\,,$$

where $V$ is the volume of the cuboid within the capacitor. This expression includes the work done by the electric field by polarizing the cuboid but not the interaction of the induced polarization with the field given by $F_{\text{int}} = -V\mathbf{E} \cdot \mathbf{P} = -VEP$ because $\mathbf{P}$ and $\mathbf{E}$ are parallel. The total free energy of the dielectric cuboid and the electric field is

$$F'(T,E) = F(T,E) + F_{\text{int}} = F(T,0) - \frac{V}{2}(\epsilon - 1)\epsilon_0 E^2.$$

The force acting on the cuboid is equal to $\mathcal{F} = -\left(\partial F'/\partial y\right)_{T,E}$, where $y$ is the displacement of the cuboid from the center of the capacitor (Fig. 4.4). We further have $V = A(a-y)$, where $A$ is the area of the cross section of the cuboid and $a$ is its length. Thus

$$\mathcal{F} = -\frac{A}{2}(\epsilon - 1)\epsilon_0 E^2.$$

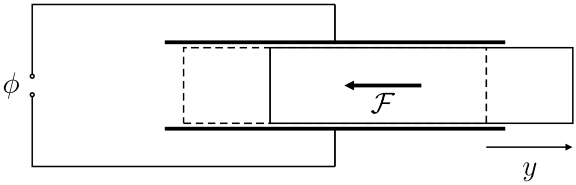

**Fig. 4.4** Force on a dielectric cuboid in a capacitor pushes the body toward center (dashed line)

The force points toward the center of the capacitor and does not depend on $y$. Consequently, the oscillations of the cuboid are not harmonic—instead, its motion toward equilibrium is characterized by constant acceleration. We have $y_0 = \mathcal{F}t_0^2/32m$, where $y_0$ and $t_0$ are the amplitude and the period of oscillations, respectively, and $m$ is the mass of the cuboid. This gives

$$t_0 = \sqrt{\frac{64my_0}{A(\epsilon - 1)\epsilon_0 E^2}} = 25.4 \text{ s}$$

and the corresponding angular frequency is 0.248 $\text{s}^{-1}$.

**Problem 4.24.**
*A sample containing* 10 g *of castor oil is placed between the plates of a capacitor and the voltage is slowly increased from* 0 to $10^8$ V/m *at constant pressure. Calculate the change of entropy of the oil! The density, thermal expansion coefficient, and relative permittivity of the oil are* 800 kg/m$^3$, $0.97 \times 10^{-3}$ K$^{-1}$, *and* 4.62, *respectively, and* $\epsilon^{-1}(\partial\epsilon/\partial T)_p = -0.0107$ K$^{-1}$.

Since the voltage is increased slowly, the process is isothermal. The change of entropy $\Delta S = \int_0^E (\partial S/\partial E)_{T,p}\,\mathrm{d}E$ depends on the derivative $(\partial S/\partial E)_{T,p}$ deduced from the total differential of the Gibbs free energy $G' = U - TS + pV - VEP$. This gives

$$\left(\frac{\partial S}{\partial E}\right)_{T,p} = \left(\frac{\partial (VP)}{\partial T}\right)_{E,p} = V(\epsilon - 1)\epsilon_0 \left[\beta + \frac{1}{\epsilon - 1}\left(\frac{\partial \epsilon}{\partial T}\right)_p\right] E$$

and finally

$$\Delta S = \frac{m(\epsilon - 1)\epsilon_0}{2\rho}\left[\beta + \frac{1}{\epsilon - 1}\left(\frac{\partial \epsilon}{\partial T}\right)_p\right] E^2 = -2.54 \times 10^{-2}\ \mathrm{J/K}\,.$$

If we neglect the expansion of oil, the result is $\Delta S = -2.73 \times 10^{-2}$ J/K.

**Problem 4.25.**

*A thin layer of globular proteins on the surface of water behaves like a two-dimensional gas. At a temperature $T$, the surface pressure of the layer is given by*

$$\gamma = Nk_BT\frac{A}{(A - N\alpha)^2}\,,$$

*where $A$ is the surface area of the layer, $N$ is the number of proteins, and $\alpha = 10^{-14}$ cm$^2$. Calculate the surface thermal expansion coefficient and the isothermal compressibility of a layer of $A = 5$ cm$^2$ and $N = 3 \times 10^{14}$ at 20 °C! In addition, find the difference of heat capacities $C_\gamma - C_A$ as well as the adiabatic compressibility of the layer! Assume that $C_A = Nk_B$.*

The thermal expansion coefficient of the layer is given by

$$\beta = \frac{1}{A}\left(\frac{\partial A}{\partial T}\right)_\gamma = \frac{1}{T}\frac{A - N\alpha}{A + N\alpha} = 8.5 \times 10^{-4}\ \mathrm{K}^{-1}$$

and the isothermal compressibility is equal to

$$\chi_T = -\frac{1}{A}\left(\frac{\partial A}{\partial \gamma}\right)_T = \frac{1}{Nk_BT}\frac{(A - N\alpha)^3}{A(A + N\alpha)} = 16.5\ \mathrm{m/N}.$$

The difference of heat capacities is calculated like in Problem 4.2:

$$C_\gamma - C_A = T\left(\frac{\partial \gamma}{\partial T}\right)_T\left(\frac{\partial A}{\partial T}\right)_\gamma = Nk_B\frac{A^2}{A^2 - (N\alpha)^2}$$
$$= 6.5 \times 10^{-9}\ \mathrm{J/K}.$$

The adiabatic compressibility is obtained from its isothermal counterpart: $\chi_S = (C_A/C_\gamma)\chi_T$; see Problem 4.9. Therefore

$$\chi_S = \frac{1}{Nk_BT}\frac{(A-N\alpha)^4}{A\left[2A^2-(N\alpha)^2\right]} = 6.4\ \mathrm{m/N}.$$

The equation of state considered here represents a gas consisting of hard disks, $\alpha$ being related to the non-ideal nature of the gas. Thus for $\alpha \to 0$ one should recover the ideal-gas behavior and indeed in this limit $\beta = 1/T$, $\chi_T = A/Nk_BT = 1/\gamma$, and $C_\gamma - C_A = Nk_B$. (Here $k_B = R/N_A$, where $N_A$ is the Avogadro number.)

**Problem 4.26.**

*The length $\ell$ of a liquid-crystal elastomer band stretched by a force $\mathcal{F}$ at a temperature $T$ is given by*

$$\frac{\ell}{\ell_0} = 1 + \frac{\mathcal{F}}{\mathcal{F}_0} + \left(1 - \frac{\mathcal{F}}{\mathcal{F}_0}\right)\tanh\left(1 - \frac{T}{T_0}\right),$$

*where $\ell_0 = 0.4\,\mathrm{m}$, $T_0 = 80\,°\mathrm{C}$, and $\mathcal{F}_0 = 2\,\mathrm{N}$. The validity of this simple phenomenological model is limited to $\mathcal{F} \lesssim \mathcal{F}_0$. Calculate the thermal expansion coefficient of the band at $T = 80\,°\mathrm{C}$ and $\mathcal{F} = 1\,\mathrm{N}$! —A stretching force of $1\,\mathrm{N}$ is applied isothermally and reversibly at $80\,°\mathrm{C}$ to a band that is initially free of constraints. How much heat is exchanged with the environment in the process? At what temperature is the heat exchanged during such a process maximal? Assume that this temperature does not differ significantly from $T_0$.*

The thermal expansion coefficient is equal to

$$\begin{aligned}\alpha &= \frac{1}{\ell}\left(\frac{\partial \ell}{\partial T}\right)_{\mathcal{F}} = \frac{1}{T_0}\frac{\ell_0}{\ell}\left(\frac{\mathcal{F}}{\mathcal{F}_0} - 1\right)\cosh^{-2}\left(1 - \frac{T}{T_0}\right)\\ &= -9.4 \times 10^{-4}\ \mathrm{K}^{-1}\end{aligned}$$

and is negative, which is a signature of rubber elasticity.

When the elastomer band is stretched isothermally and reversibly, the heat exchanged with the environment at $T = T_0$ is

$$\begin{aligned}Q &= T\int_0^{\mathcal{F}}\left(\frac{\partial S}{\partial \mathcal{F}}\right)_T \mathrm{d}\mathcal{F} = T\int_0^{\mathcal{F}}\left(\frac{\partial \ell}{\partial T}\right)_{\mathcal{F}} \mathrm{d}\mathcal{F}\\ &= -\ell_0\left(\mathcal{F} - \frac{\mathcal{F}^2}{2\mathcal{F}_0}\right)\frac{T}{T_0}\cosh^{-2}\left(1 - \frac{T}{T_0}\right) = -0.30\ \mathrm{J}.\end{aligned}$$

Heat is released by the band; the phenomenon is known as the elastocaloric effect. From the above equations we see that the heat exchanged depends on the temperature at which the isothermal stretching is performed. The maximum of the heat exchanged is determined by $\mathrm{d}Q/\mathrm{d}T = 0$, which leads to a transcendental equation for $T$:

$$1 + \frac{2T}{T_0}\tanh\left(1 - \frac{T}{T_0}\right) = 0.$$

As we expect that the maximum is at a temperature that is not too different from $T_0$, we expand the hyperbolic tangent to first order and obtain a quadratic equation for $T/T_0$

$$\left(\frac{T}{T_0}\right)^2 - \frac{T}{T_0} - \frac{1}{2} = 0\,,$$

with the physically meaningful solution $T/T_0 = (1+\sqrt{3})/2 \approx 1.3660$ or $T = 209\,°\mathrm{C}$. We notice that the obtained temperature is actually not very close to $T_0$ as assumed, yet it still agrees well with the exact solution of the transcendental equation which is $T/T_0 \approx 1.3797$.

# Chapter 5
# Phase Transitions

**Problem 5.1.**
*At* $0\,^\circ\mathrm{C}$ *and* $1$ bar, *the heat of fusion of ice is* $336\,\mathrm{kJ/kg}$ *and its density is* $917\,\mathrm{kg/m^3}$; *the saturated water vapor pressure at* $0\,^\circ\mathrm{C}$ *is* $6.1$ mbar *and the heat of vaporization is* $2.50\,\mathrm{MJ/kg}$. *Using these data, calculate the location of the triple point of water!*

In the vicinity of the triple point, phase coexistence in the temperature–pressure phase diagram can be represented by straight lines of slopes given by the Clausius–Clapeyron equation, the reference points being $0\,^\circ\mathrm{C}$ and 1 bar for the coexistence of ice and liquid water and $0\,^\circ\mathrm{C}$ and 6.1 mbar for the coexistence of liquid water and vapor. (As one can deduce from Fig. 5.1, the latter can only be metastable given that it is located in the region where ice turns out to be the only stable phase.) The ice–water coexistence is described by

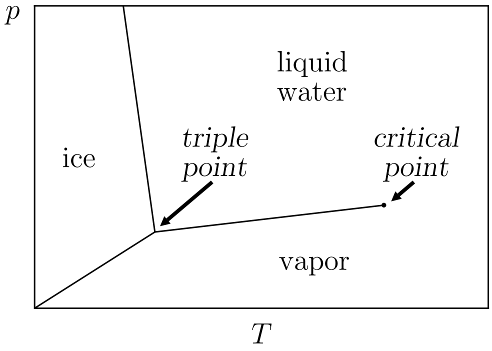

**Fig. 5.1** Phase diagram of water. Since the density of ice is lower than that of liquid water, the slope of the water–ice coexistence line is negative

G. Skačej and P. Ziherl, *Solved Problems in Thermodynamics and Statistical Physics*, https://doi.org/10.1007/978-3-030-27661-4_5

$$\begin{aligned} p_{sl}(T) &= p_{sl}(T_0) + \left.\frac{\mathrm{d}p_{sl}}{\mathrm{d}T}\right|_{T=T_0}(T - T_0) \\ &= p_{sl}(T_0) + \frac{q_f}{T_0\,(1/\rho_l - 1/\rho_s)}(T - T_0) \end{aligned}$$

whereas at the water–vapor coexistence

$$\begin{aligned} p_{lv}(T) &= p_s(T_0) + \left.\frac{\mathrm{d}p_{lv}}{\mathrm{d}T}\right|_{T=T_0}(T - T_0) \\ &= p_s(T_0) + \frac{q_v}{T_0\,(1/\rho_v - 1/\rho_l)}(T - T_0) \\ &\approx p_s(T_0) + \frac{p_s(T_0)Mq_v}{RT_0^2}(T - T_0)\,. \end{aligned}$$

Here, we took into account that the density of vapor is much lower than that of water and we expressed it using the ideal-gas equation of state. The phase coexistence lines meet at 0.0075 °C and 6.1 mbar. Due to air dissolved in water which lowers the melting point, the true triple point of water is at a slightly higher temperature of 0.01 °C.

**Problem 5.2.**
*A vessel contains* 2 l *of liquid water and* 1 l *of vapor at* 20 °C. *Calculate the volumetric thermal expansion coefficient of the system if water–vapor coexistence is maintained! The equation of state for liquid water reads*

$$V_l = \frac{m_l}{\rho_0}\left[1 - \chi_l p + \beta_l\,(T - T_0)\right],$$

*where* $\rho_0 = 998\ \mathrm{kg/m^3}$, $\chi_l = 4.6 \times 10^{-10}\ \mathrm{Pa^{-1}}$, $\beta_l = 2.06 \times 10^{-4}\ \mathrm{K^{-1}}$, *and* $T_0 = 273$ K. *The heat of vaporization is* 2.45 MJ/kg, *the kilomolar mass is* 18 kg/kmol, *and the saturated vapor pressure at* 20 °C is 23.4 mbar.

Because the system is rather far from the critical point, the density of water $\rho_l$ is much higher than that of vapor $\rho_v$. In this case, the Clausius–Clapeyron equation can be simplified to read

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{q_v}{T\,(1/\rho_v - 1/\rho_l)} \approx \frac{\rho_v q_v}{T} = \frac{pMq_v}{RT^2}\,.$$

This gives the temperature dependence of pressure, where liquid water and vapor coexist. Now we consider the variation of vapor volume $V_v$ with temperature:

$$\left(\frac{\partial V_v}{\partial T}\right)_\mu = \left(\frac{\partial V_v}{\partial T}\right)_p + \left(\frac{\partial V_v}{\partial p}\right)_T \frac{\mathrm{d}p}{\mathrm{d}T} = \frac{V_v}{T}\left(1 - \frac{Mq_v}{RT}\right).$$

(The subscript $\mu$ indicates that the chemical potentials of water and vapor are equal.) This derivative is negative because upon heating, the volume decrease due to the increase of saturated pressure exceeds the volume increase observed at constant pressure. For liquid water, we have

$$\left(\frac{\partial V_l}{\partial T}\right)_\mu = \left(\frac{\partial V_l}{\partial T}\right)_p + \left(\frac{\partial V_l}{\partial p}\right)_T \frac{\mathrm{d}p}{\mathrm{d}T} = \frac{m_l}{\rho_0}\beta_l\left(1 - \frac{\chi_l}{\beta_l}\frac{pMq_v}{RT^2}\right).$$

After evaluating the two derivatives, we find that $(\partial V_l/\partial T)_\mu \ll (\partial V_v/\partial T)_\mu$ and one has

$$\beta_\mu = \frac{1}{V_v + V_l}\left(\frac{\partial(V_v + V_l)}{\partial T}\right)_\mu \approx \frac{1}{V_v + V_l}\left(\frac{\partial V_v}{\partial T}\right)_\mu = -0.0193\ \mathrm{K}^{-1}.$$

**Problem 5.3.**
*A vertical* 11 cm-*tall sealed tube contains a* 10 cm *column of water and air at* 1 bar; *the temperature is* 0 °C. *Find the thickness of ice formed after the tube is cooled by* $10^{-4}$°C*! The densities of ice and water are* 917 kg/m$^3$ *and* 1000 kg/m$^3$, *respectively, and the heat of fusion is* 336 kJ/kg. *Assume that ice does not stick to the tube.*

Although the final temperature of the system is below 0 °C, not all of the water freezes because ice has a larger specific volume than water. As a result, the volume of air is decreased upon cooling and consequently the pressure inside the tube is increased. Mass conservation upon phase transition gives $h_l\rho_l = h_s\rho_s$, where $h_l$ and $h_s$ denote the height of the columns of water that freezes and the thickness of ice, respectively (Fig. 5.2); $\rho_l$ and $\rho_s$ are the densities of water and ice, respectively. For the air column, we have $(p + \Delta p)(h_g - \Delta h_g)/(T + \Delta T) = ph_g/T$ (where $h_g$ is

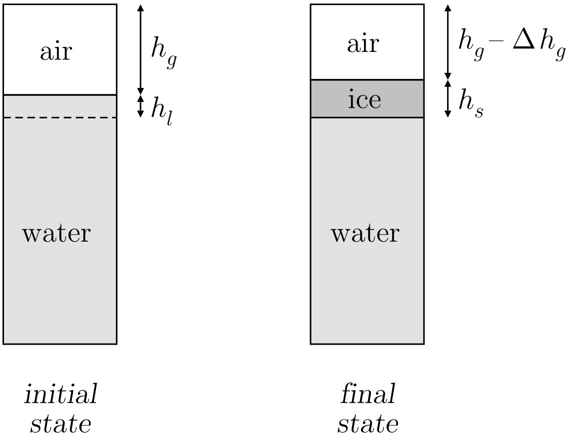

**Fig. 5.2** Given the small compressibility of liquid water, the total volume of air and ice upon cooling equals the combined initial volume of air and of water that freezes

its initial height and $\Delta h_g$ is the change of height upon cooling) or approximately $(p + \Delta p)(h_g - \Delta h_g) = ph_g$ since the temperature change is small. Thus

$$\Delta h_g = h_g \frac{\Delta p/p}{1 + \Delta p/p} .$$

As nothing happens to water that does not freeze, the combined height of the column of water that does freeze and of the air column is conserved: $h_l + h_g = h_s + h_g - \Delta h_g$. Therefore

$$\Delta h_g = h_s \left(1 - \frac{\rho_s}{\rho_l}\right) .$$

Finally, we find that

$$h_s = \frac{h_g}{1 - \rho_s/\rho_l} \frac{\Delta p/p}{1 + \Delta p/p} = 1.61 \text{ mm} ,$$

with $\Delta p = q_f \Delta T \big/ \left[T \left(1/\rho_l - 1/\rho_s\right)\right]$ according to the Clausius–Clapeyron equation.

**Problem 5.4.**
*What is the derivative of the heat of vaporization of water with respect to temperature close to the boiling point at standard atmospheric pressure? At* 100 °C, *the heat capacities of water vapor and liquid water at constant pressure are* 1890 J/kgK *and* 4210 J/kgK, *respectively.*

We start with a more general discussion of the temperature dependence of the latent heat given by $q = T(s_2 - s_1)$, where $s_1$ and $s_2$ are the specific entropies of the low- and the high-temperature phase, respectively. From here, $\mathrm{d}q/\mathrm{d}T = s_2 - s_1 + T\,(\mathrm{d}s_2/\mathrm{d}T - \mathrm{d}s_1/\mathrm{d}T) = q/T + T\,(\mathrm{d}s_2/\mathrm{d}T - \mathrm{d}s_1/\mathrm{d}T)$. Since also $\mathrm{d}s = (\partial s/\partial T)_p\,\mathrm{d}T + (\partial s/\partial p)_T\,\mathrm{d}p = (c_p/T)\,\mathrm{d}T - m^{-1}\,(\partial V/\partial T)_p\,\mathrm{d}p$ and $m^{-1}\,(\partial V/\,\partial T)_p = \beta/\rho$, we obtain $\mathrm{d}q/\mathrm{d}T = q/T + c_{p2} - c_{p1} - T\,(\beta_2/\rho_2 - \beta_1/\rho_1)\,\mathrm{d}p/\mathrm{d}T$. Along the phase equilibrium we have $\mathrm{d}p/\mathrm{d}T = q/\left[T(1/\rho_2 - 1/\rho_1)\right]$, hence

$$\frac{\mathrm{d}q}{\mathrm{d}T} = \frac{q}{T} + c_{p2} - c_{p1} - \left(\frac{\beta_2}{\rho_2} - \frac{\beta_1}{\rho_1}\right) \frac{q}{1/\rho_2 - 1/\rho_1} .$$

For liquid–gas transition far from the critical point, $\rho_2 \ll \rho_1$ holds and, in a rarefied gas, $\beta_2 \approx 1/T$ can further be assumed. In this case $\mathrm{d}q/\mathrm{d}T = c_{p2} - c_{p1}$. For the water–vapor transition close to the boiling point at 1 bar we obtain $\mathrm{d}q/\mathrm{d}T = -2320$ J/kgK.

**Problem 5.5.**
*A tall vertical tube at* 250 K *is filled with a column which is solid at the bottom, whereas its top part is liquid; the heat of fusion is* 147 kJ/kg. *Upon cooling the column by* $10^{-3}$ K, *the solid–liquid interface moves by* 1 m. *Does it move up or*

*down? What is the ratio of densities of the liquid and the solid phase? Assume that thermal expansion is negligible.*

Given that the solid phase is found at the bottom of the tube where, due to gravity, it is exposed to a higher pressure than the liquid phase at the top, the phase coexistence curve in the phase diagram is characterized by $\mathrm{d}p/\mathrm{d}T > 0$. Therefore, upon cooling by $\Delta T$, the equilibrium is shifted to a lower pressure and thus the interface moves up by $\Delta h$ (Fig. 5.3). The density ratio is obtained from the Clausius–Clapeyron equation which reads

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{q_f}{T\left(\rho_l^{-1} - \rho_s^{-1}\right)} = \frac{\rho_l g \Delta h}{\Delta T}\,,$$

where $q_f$ stands for the heat of fusion, $\rho_l$ and $\rho_s$ denote the densities of the liquid and the solid phase, respectively, $g$ is the gravitational acceleration, and $T$ is temperature. We find that

$$\frac{\rho_l}{\rho_s} = 1 - \frac{q_f}{g\Delta h}\frac{\Delta T}{T} = 0.94\,.$$

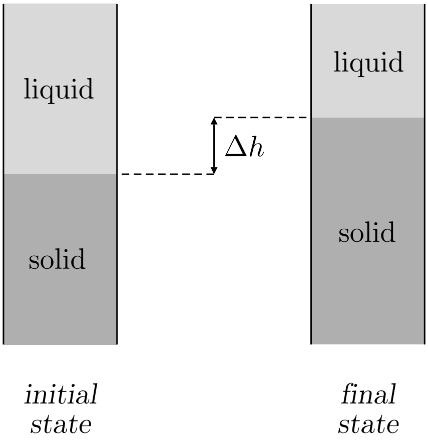

**Fig. 5.3** Tall column in gravitational field: Upon cooling, the liquid-solid interface moves up by $\Delta h$

### Problem 5.6.

*Upon heating a sample of iron at* 1 bar, *one observes a transition from phase* $\alpha$ *to phase* $\gamma$ *at* 900 °C. *As the sample is further heated at constant pressure, it undergoes a re-entrant transition to phase* $\alpha$ *at* 1400 °C. *The heat capacity of phases* $\alpha$ *and* $\gamma$ *are* 775 J/kgK *and* 690 J/kgK, *respectively. Calculate the heat of fusion of the two transitions!*

Assume that iron is heated from $T_1 = 900\,°\mathrm{C}$ to $T_2 = 1400\,°\mathrm{C}$ in two ways: In the first case, the sample remains in phase $\alpha$, whereas in the second it first experiences a transition to phase $\gamma$ at $T_1$ and then it is heated to $T_2$ where it switches back to phase $\alpha$. In the first case, the change of enthalpy is given by

$$H_\alpha(T_2) - H_\alpha(T_1) = mc_p^\alpha\,(T_2 - T_1)\ ,$$

and the change of entropy is

$$S_\alpha(T_2) - S_\alpha(T_1) = mc_p^\alpha \ln\frac{T_2}{T_1}\ ;$$

here $c_p^\alpha$ stands for the heat capacity of phase $\alpha$ and $m$ is the mass of the sample. In the second case we have

$$H_\alpha(T_2) - H_\alpha(T_1) = mq(T_1) + mc_p^\gamma\,(T_2 - T_1) + mq(T_2)$$

and

$$S_\alpha(T_2) - S_\alpha(T_1) = \frac{mq(T_1)}{T_1} + mc_p^\gamma \ln\frac{T_2}{T_1} + \frac{mq(T_2)}{T_2}\ ,$$

where $q(T)$ is the heat of fusion and $c_p^\gamma$ is the heat capacity of phase $\gamma$. Both enthalpy and entropy are functions of state; as a consequence, the change of these quantities does not depend on how the sample was heated. Therefore

$$q(T_1) = T_1\left(c_p^\alpha - c_p^\gamma\right)\left[\frac{T_2\ln\left(T_1/T_2\right)}{T_1 - T_2} - 1\right];$$

for $q(T_2)$ we obtain the same expression with indices 1 and 2 interchanged. Finally we have $q(T_1) = 18.7$ kJ/kg and $q(T_2) = -23.7$ kJ/kg.

**Problem 5.7.**
*Calculate the heat of vaporization of the van der Waals fluid at* $T = 0$*!*

Mechanical equilibrium requires that the pressures of the liquid and the vapor phase be equal: $\mathcal{P}_v = \mathcal{P}_l$ or $8\mathcal{T}/(3\mathcal{V}_l - 1) - 3/\mathcal{V}_l^2 = 8\mathcal{T}/(3\mathcal{V}_v - 1) - 3/\mathcal{V}_v^2$; here we use the dimensionless form of the van der Waals equation of state (Problem 1.1). At very low temperatures, we have $\mathcal{V}_l \approx 1/3$ and $\mathcal{V}_v \gg 1$, hence this condition can be replaced by $8\mathcal{T}/(3\mathcal{V}_l - 1) - 27 = 0$. From here it follows that $\mathcal{V}_l - 1/3 \approx 8\mathcal{T}/81$.

The Maxwell rule which determines the saturated vapor pressure states that

$$\int_{\mathcal{V}_l}^{\mathcal{V}_v} \mathcal{P}\,\mathrm{d}\mathcal{V} = \mathcal{P}_s(\mathcal{V}_v - \mathcal{V}_l)\,.$$

The integral on the left-hand side is equal to $(8\mathcal{T}/3)\ln\big((3\mathcal{V}_v-1)/(3\mathcal{V}_l-1)\big)+3\,(1/\mathcal{V}_v-1/\mathcal{V}_l)\approx(8\mathcal{T}/3)\ln\big(3\mathcal{V}_v/(3\mathcal{V}_l-1)\big)-9$ because $\mathcal{V}_l\approx 1/3$ and $\mathcal{V}_v\gg 1$, whereas the right-hand side is approximately equal to $8\mathcal{T}/3$ and thus approaches 0 at low temperatures. Thus $\mathcal{V}_v\approx(\mathcal{V}_l-1/3)\exp(27/8\mathcal{T})$, and, upon inserting the relation $\mathcal{V}_l-1/3\approx 8\mathcal{T}/81$ obtained from the condition of mechanical equilibrium, we finally have $\mathcal{V}_v=(8\mathcal{T}/81)\exp(27/8\mathcal{T})$ (Fig. 5.4). Hence

$$\mathcal{P}_s\approx\frac{8\mathcal{T}}{3\mathcal{V}_v}=27\exp\left(-\frac{27}{8\mathcal{T}}\right),$$

which is illustrated in Fig. 5.5. At this point, the heat of vaporization is just a step away. By substituting $\mathcal{V}_v-\mathcal{V}_l\approx\mathcal{V}_v$ into the Clausius–Clapeyron equation, we find that

$$q_v\approx\frac{p_cV_{Mc}}{M}\mathcal{T}\mathcal{V}_v\frac{\mathrm{d}\mathcal{P}_s}{\mathrm{d}\mathcal{T}}=\frac{9p_cV_{Mc}}{M},$$

which agrees well with the exact numerical result (Fig. 5.6).

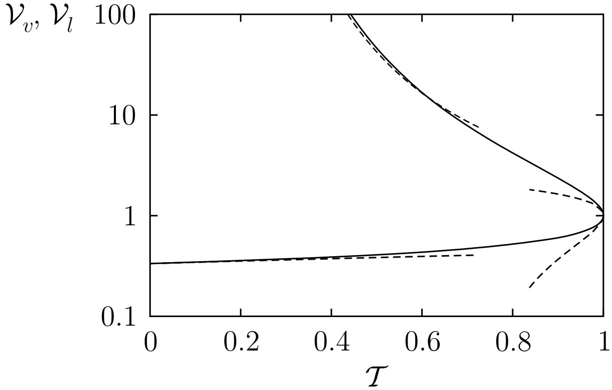

**Fig. 5.4** Liquid–gas coexistence in the van der Waals fluid: Exact reduced volumes of the gas and the liquid phase plotted vs. reduced temperature (solid line) and the low- and high-temperature approximations (dashed lines). The behavior close to $\mathcal{T}=1$ is discussed in Problem 5.8, which also applies to Figs. 5.5 and 5.6

### Problem 5.8.

*Calculate the heat of vaporization for a van der Waals fluid close to the critical point! What is the heat of vaporization of carbon dioxide at* 25 °C*? The critical pressure is* 73 bar, *the critical kilomolar volume is* $0.095\,\mathrm{m}^3/\mathrm{kmol}$, *and the critical temperature is* 31 °C.

We write $\mathcal{P}=1+\mathcal{X}$, $\mathcal{V}=1+\mathcal{Y}$, and $\mathcal{T}=1+\mathcal{Z}$, where $\mathcal{X},\mathcal{Y},\mathcal{Z}\ll 1$, and recast the dimensionless van der Waals equation of state from Problem 1.1 as

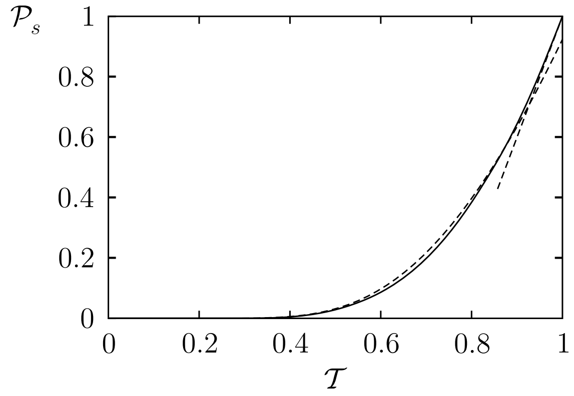

**Fig. 5.5** Saturated vapor pressure in a van der Waals gas (solid line) and the corresponding low- and high-temperature approximations (dashed lines). The low-temperature approximation fits the exact $\mathcal{P}_s(\mathcal{T})$ quite well at all temperatures—even at the critical temperature, the relative difference is merely 7.6%

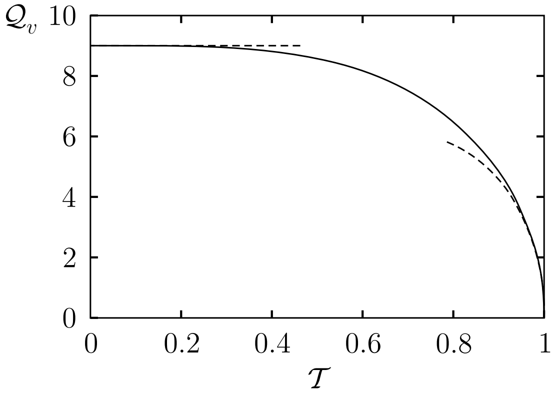

**Fig. 5.6** Heat of vaporization of the van der Waals fluid expressed in reduced units where $\mathcal{Q}_v = Mq_v/p_cV_{Mc}$ (solid line) and its low- and high-temperature approximations (dashed lines)

$$\mathcal{X} = -\frac{3}{2}\mathcal{Y}^3 + 4\mathcal{Z} - 6\mathcal{Y}\mathcal{Z}\,.$$

Mechanical equilibrium requires that $\mathcal{X}_l = \mathcal{X}_v = \mathcal{X}_s$ or $-3\mathcal{Y}_l^3/2 - 6\mathcal{Y}_l\mathcal{Z} = -3\mathcal{Y}_v^3/2 - 6\mathcal{Y}_v\mathcal{Z}$, and in terms of reduced variables, the chemical equilibrium is given by $\int_{\mathcal{Y}_l}^{\mathcal{Y}_v}\mathcal{X}\mathrm{d}\mathcal{Y} = \mathcal{X}_s(\mathcal{Y}_v - \mathcal{Y}_l)$. After we evaluate the integral, we obtain $-(3/8)(\mathcal{Y}_v^4 - \mathcal{Y}_l^4) + 4\mathcal{Z}(\mathcal{Y}_v - \mathcal{Y}_l) - 3\mathcal{Z}(\mathcal{Y}_v^2 - \mathcal{Y}_l^2) = \mathcal{X}_s(\mathcal{Y}_v - \mathcal{Y}_l)$ or $\mathcal{X}_s = -(3/8)(\mathcal{Y}_v^2 + \mathcal{Y}_l^2)(\mathcal{Y}_v + \mathcal{Y}_l) + 4\mathcal{Z} - 3\mathcal{Z}(\mathcal{Y}_v + \mathcal{Y}_l)$. The saturated vapor pressure must be equal to

$\mathcal{X}(\mathcal{Y}_l) = -3\mathcal{Y}_l^3/2 + 4\mathcal{Z} - 6\mathcal{Y}_l\mathcal{Z}$ and $\mathcal{X}(\mathcal{Y}_v) = -3\mathcal{Y}_v^3/2 + 4\mathcal{Z} - 6\mathcal{Y}_v\mathcal{Z}$. The sum of the ensuing two equations reduces to $(\mathcal{Y}_v - \mathcal{Y}_l)^2(\mathcal{Y}_v + \mathcal{Y}_l) = 0$. Apparently, $\mathcal{Y}_v = -\mathcal{Y}_l$ so that $\mathcal{Y}_l = -2\sqrt{-\mathcal{Z}}$, $\mathcal{Y}_v = 2\sqrt{-\mathcal{Z}}$, and $\mathcal{X}_s = 4\mathcal{Z}$ or

$$\begin{aligned}\mathcal{V}_l &= 1 - 2\sqrt{1-\mathcal{T}}\,,\\ \mathcal{V}_v &= 1 + 2\sqrt{1-\mathcal{T}}\,, \quad \text{and}\\ \mathcal{P}_s &= 4\mathcal{T} - 3\,.\end{aligned}$$

Figure 5.4 shows $\mathcal{V}_l$ and $\mathcal{V}_v$ as functions of temperature and $\mathcal{P}_s$ is plotted in Fig. 5.5. These results can be used to calculate the critical exponent for the order parameter, which is given by the difference of the densities of the liquid and gas phase in coexistence. We have $\rho_l - \rho_v \propto \mathcal{V}_l^{-1} - \mathcal{V}_v^{-1} \propto \sqrt{T_c - T}$ so that the critical exponent $\beta = 1/2$, which agrees with the mean-field approximation.

The heat of vaporization follows from the Clausius–Clapeyron equation and reads

$$q_v = \frac{p_c V_{Mc}}{M}\mathcal{T}(\mathcal{V}_v - \mathcal{V}_l)\frac{\mathrm{d}\mathcal{P}_s}{\mathrm{d}\mathcal{T}} = 16\frac{p_c V_{Mc}}{M}\frac{T}{T_c}\sqrt{1-\frac{T}{T_c}}\,;$$

its temperature dependence is depicted in Fig. 5.6. The heat of vaporization for carbon dioxide at 25 °C is 34.7 kJ/kg.

**Problem 5.9.**

*Calculate the critical exponent characterizing the difference of heat capacities $c_p - c_V$ in the van der Waals fluid if the critical point is approached at the critical pressure! How does the result change if the critical point is approached at the critical volume? Calculate the adiabatic compressibility at the critical point!*

Like in Problem 5.8 we put $\mathcal{P} = 1 + \mathcal{X}$, $\mathcal{V} = 1 + \mathcal{Y}$, and $\mathcal{T} = 1 + \mathcal{Z}$ with $\mathcal{X}$, $\mathcal{Y}$, and $\mathcal{Z} \ll 1$. By inserting these expressions into the dimensionless van der Waals equation of state, we have $\left[1 + \mathcal{X} + 3/(1+\mathcal{Y})^2\right](2 + 3\mathcal{Y}) = 8(1 + \mathcal{Z})$. By taking into account that $(1+u)^{-2} = 1 - 2u + 3u^2 - 4u^3 + \ldots$ and keeping the terms up to third order in $\mathcal{Y}$, we are left with

$$3\mathcal{Y}^3 + (2 + 3\mathcal{Y})\mathcal{X} - 8\mathcal{Z} = 0\,.$$

(One can quickly verify that the above approximate form of the van der Waals equation of state is equivalent to the one in Problem 5.8.) At the critical temperature, the difference of heat capacities $c_p - c_V = (T/m)\,(\partial p/\partial T)_V\,(\partial V/\partial T)_p$ is equal to $(3R/8M)\,(\partial\mathcal{P}/\partial\mathcal{T})_{\mathcal{V}}\,(\partial\mathcal{V}/\partial\mathcal{T})_{\mathcal{P}}$; here we used the relation $p_c V_{Mc}/M T_c = 3R/8M$. From the approximate form of the equation of state, we have $(\partial\mathcal{P}/\partial\mathcal{T})_{\mathcal{V}} = 8/(2 + 3\mathcal{Y})$ and $(\partial\mathcal{V}/\partial\mathcal{T})_{\mathcal{P}} = 8/\left[3(\mathcal{X} + 3\mathcal{Y}^2)\right]$ so that, in turn, $c_p - c_V \approx 8R/M(2 + 3\mathcal{Y})(\mathcal{X} + 3\mathcal{Y}^2)$.

At the critical pressure $\mathcal{X} = 0$, $\mathcal{Y} = (8\mathcal{Z}/3)^{1/3}$ and thus

$$c_p - c_V \approx \frac{4R}{3M\mathcal{Y}^2} \propto \mathcal{Z}^{-2/3} \propto (T/T_c - 1)^{-2/3}$$

so that the critical exponent of interest is $2/3$.

On the other hand, at the critical volume $\mathcal{Y} = 0$ we have $\mathcal{X} = 4\mathcal{Z}$ and

$$c_p - c_V \approx \frac{R}{M\mathcal{Z}} \propto \mathcal{Z}^{-1} \propto (T/T_c - 1)^{-1}.$$

In this case the critical exponent is equal to 1.

The adiabatic compressibility is calculated from $\chi_S = (c_V/c_p)\chi_T$. Given that $c_p - c_V$ diverges at the critical point, $c_p/c_V$ can be estimated by $\left(c_p - c_V\right)/c_V = (8R/Mc_V)\left[(2+3\mathcal{Y})(\mathcal{X}+3\mathcal{Y}^2)\right]^{-1}$, whereas the isothermal compressibility is $\chi_T = p_c^{-1}(2+3\mathcal{Y})/\left[3(\mathcal{X}+3\mathcal{Y}^2)\right]$. Therefore

$$\chi_S \approx \frac{Mc_V}{24Rp_c}(2+3\mathcal{Y})^2\,,$$

which does not diverge at the critical point.

**Problem 5.10.**
*Explore the behavior of magnetization and heat capacity near the ferromagnetic–paramagnetic transition within the Landau theory! Calculate the critical exponents of the order parameter and the heat capacity!*

The Landau Gibbs free energy for magnetic systems per unit mass (below referred to as the free energy for brevity) is given by

$$g(M,T) = g(0,T) + a(T-T_c)\frac{M^2}{2} + b\frac{M^4}{4}\,,$$

where $g(0,T)$ is the free energy in absence of magnetization $M$ at a temperature $T$, $a$ and $b$ are positive constants, and $T_c$ is the phase transition temperature (Fig. 5.7). The equilibrium magnetization corresponds to the minimum of the free energy given by $(\partial g/\partial M)_T = a(T-T_c)M + bM^3 = 0$. This equation has two solutions: $M = 0$ represents the paramagnetic phase with the free energy of $g(0,T)$, whereas $M = \pm\sqrt{a(T_c-T)/b}$ represents the ferromagnetic phase which exists only for $T < T_c$ and where the free energy is $g(0,T) - a^2(T-T_c)^2/4b$. The paramagnetic and the ferromagnetic phase are stable above and below $T_c$, respectively. After we introduce the dimensionless temperature $\mathcal{T} = (T-T_c)/T_c$, we immediately see that the critical exponent of the order parameter (i.e., magnetization) defined by $M(\mathcal{T} < 0) \propto (-\mathcal{T})^\beta$ is equal to $\beta = 1/2$.

The heat capacity $c$ is calculated from $c = T\,\mathrm{d}s/\mathrm{d}T = -\mathrm{d}^2g/\mathrm{d}T^2$, and we find that $c_{M=0} = -T\,\mathrm{d}^2g(0,T)/\mathrm{d}T^2$ in the paramagnetic phase and $c_{M\neq 0} = c_{M=0} + a^2T/2b$ in the ferromagnetic phase. As $c_{M\neq 0} - c_{M=0}$ does not diverge at the transition, the critical exponent of the heat capacity $\alpha = 0$.

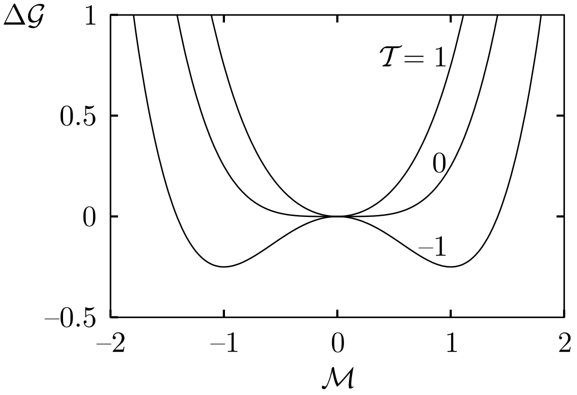

**Fig. 5.7** Landau theory of the ferromagnetic–paramagnetic transition: The Gibbs free energy [per unit mass; relative to $g(0, T)$ and plotted in units of $(aT_c)^2/b$] as a function of reduced magnetization $\mathcal{M} = M/(aT_c/b)^{1/2}$ at reduced temperature $\mathcal{T} = (T - T_c)/T_c = -1, 0$, and 1. Above the critical temperature corresponding to $\mathcal{T} = 0$ the minimum is at $\mathcal{M} = 0$, whereas below the critical temperature there exist two minima at $\mathcal{M} = \pm\sqrt{-\mathcal{T}}$

**Problem 5.11.**

*Calculate the magnetic susceptibilities of the paramagnetic and the ferromagnetic phase within the Landau theory!*

To describe the coupling of magnetization to the magnetic field, we extend the Gibbs free energy per unit volume from Problem 5.10 by

$$-\frac{\mu_0 HM}{\rho}\,,$$

where $H$ and $\rho$ denote the magnetic field strength and the density of the sample, respectively. In the paramagnetic phase, spontaneous magnetization vanishes; therefore, the fourth-order term in the free energy can be neglected because the induced magnetization $M_i$ is small as long as the external field is weak: $g(M_i, T) = g(0, T) + a(T - T_c)M_i^2/2 - \mu_0 HM_i/\rho$. In equilibrium one has $(\partial g/\partial M_i)_T = a(T - T_c)M_i - \mu_0 H/\rho = 0$ which results in

$$M_i(T > T_c) = \frac{\mu_0}{\rho a(T - T_c)}H\,.$$

This is the Curie–Weiss law. In the ferromagnetic phase, both spontaneous and induced magnetizations exist: $M(T < T_c, H) = M_s(T) + M_i(T, H)$. In equilibrium one has $(\partial g/\partial M)_T = a(T - T_c)M + bM^3 - \mu_0 H/\rho \approx a(T - T_c)M_s + bM_s^3 + a(T - T_c)M_i + 3bM_s^2 M_i - \mu_0 H/\rho = 0$, where we assumed that $M_i \ll M_s$. As $a(T - T_c) + bM_s^2 = 0$, we obtain

$$M_i(T < T_c) = \frac{\mu_0}{2\rho a(T_c - T)} H\,.$$

The susceptibility of the paramagnetic phase at $T_c + \Delta T$ is twice as large as the susceptibility of the ferromagnetic phase at $T_c - \Delta T$. We also observe that the critical exponent of susceptibility $\gamma = 1$ in both phases (Fig. 5.8).

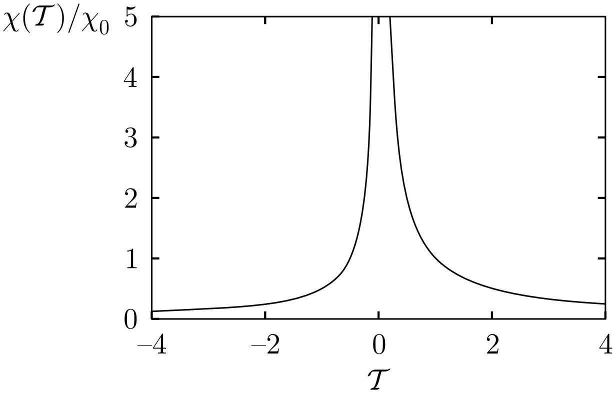

**Fig. 5.8** Susceptibilities of the ferromagnetic ($\mathcal{T} < 0$) and paramagnetic phase ($\mathcal{T} > 0$) in the units of $\chi_0 = \mu_0/\rho a T_c$ vs. reduced temperature $\mathcal{T} = (T - T_c)/T_c$. The Landau theory predicts the same value of the critical exponent below and above the transition but a larger magnitude of the susceptibility in the paramagnetic phase; $\chi(+|\mathcal{T}|) = 2\chi(-|\mathcal{T}|)$

### Problem 5.12.

*A sample of ferromagnetic iron is placed into a magnetic field of* $10^6$ A/m *strength which is antiparallel to the existing spontaneous magnetization. Up to which temperature must the sample be heated in order to reverse the direction of the magnetization? Use the Landau theory and treat the magnetization as a scalar. The ferromagnetic–paramagnetic transition is at* 770 °C. *At* 800 °C *the susceptibility of the sample is* 0.007 *and at* 20 °C *its spontaneous magnetization is equal to* $1.36 \times 10^5$ A/m; *the density of the sample is* 7800 kg/m$^3$.

In absence of magnetic field, the two minima of Gibbs free energy $g(M, T) = g(0, T) + a(T - T_c)M^2/2 + bM^4/4 - \mu_0 HM/\rho$ at $T < T_c$ are equally deep (Fig. 5.7). Once the field is applied, this is no longer the case; a field along the direction corresponding to $M > 0$ makes the $M < 0$ minimum shallower than the other one and hence metastable (Fig. 5.9).

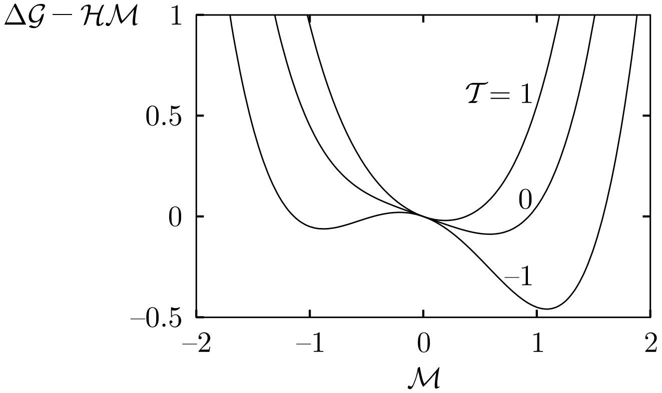

**Fig. 5.9** Landau theory Gibbs free energy of a magnetic material in a field of reduced strength of $\mathcal{H} = \mu_0 b^{1/2} H/\rho(aT_c)^{3/2} = 0.2$ [per unit mass; relative to $g(0, T)$ and plotted in units of $(aT_c)^2/b$] vs. reduced magnetization $\mathcal{M}$ at $\mathcal{T} = -1, 0$, and 1. The ferromagnetic minima are not equally deep; the one at $\mathcal{M} < 0$ is metastable and vanishes in a strong enough field. Due to the field, the paramagnetic minimum is shifted to a finite but small $\mathcal{M} > 0$

The magnetizations of the stable and the metastable phase are determined by the equation

$$a(T - T_c)M + bM^3 = \frac{\mu_0 H}{\rho}$$

which possesses three roots at a low enough $T < T^*(H) < T_c$ (the middle one belonging to the local maximum of the free energy as shown in Fig. 5.9) and only one root otherwise (Figs. 5.10 and 5.11). The highest superheating temperature of the ferromagnet with magnetization pointing opposite to the field is reached when in the equation of state, the height of the $\mathcal{M} < 0$ maximum equals $\mu_0 H/\rho$ (Fig. 5.10).

Then one has $M^* = -\sqrt{a(T_c - T^*)/3b}$ as well as $a(T^* - T_c)M^* + bM^{*3} = 2b\sqrt{a(T_c - T^*)/3b}^3 = \mu_0 H/\rho$. Thus we obtain

$$T^* = T_c - \frac{3b^{1/3}}{a}\left(\frac{\mu_0 H}{2\rho}\right)^{2/3} .$$

Let us also calculate the values of the parameters of the Landau free energy. From the susceptibility of the paramagnetic phase at 800 °C we find that $a = \mu_0/\rho\chi_p(T)(T - T_c) = 7.67 \times 10^{-10}$ Jm$^2$/kgKA$^2$, whereas from the spontaneous magnetization of the ferromagnetic phase at 20 °C we have $b = a(T_c - T)/M^2(T) = 3.11 \times 10^{-17}$ Jm$^4$/kgA$^4$. Finally, we get $T^* = T_c - 22.9$ K $= 747.1\,^\circ$ C.

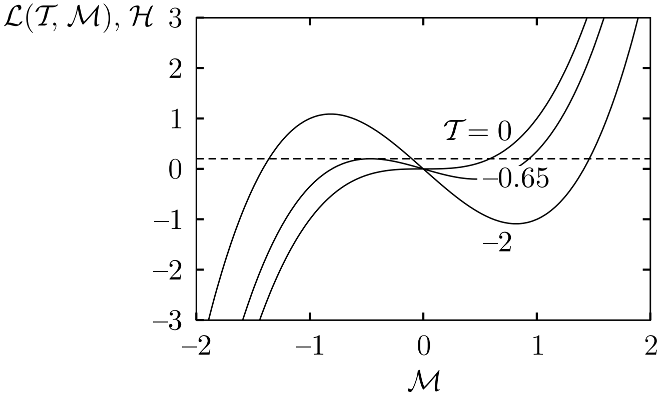

**Fig. 5.10** Solutions of the equation of equilibrium of the Landau theory in external field: In reduced units, the left-hand side $\mathcal{L}(\mathcal{T},\mathcal{M})$ reads $\mathcal{T}\mathcal{M}+\mathcal{M}^3$ (solid lines; $\mathcal{T}=-2, -0.65$, and 0), and the right-hand side is equal to $\mathcal{H}$ (dashed line; here $\mathcal{H}=0.2$). At a low enough temperature (for $\mathcal{H}=0.2$ depicted here, below $\mathcal{T}\approx -0.65$), there exist three roots, and otherwise there is just one

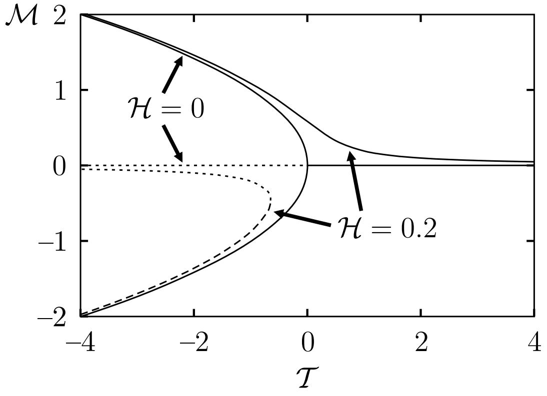

**Fig. 5.11** Landau theory of ferromagnetism: Temperature dependence of reduced magnetization in a magnetic field, here at the reduced field strength $\mathcal{H}=0.2$. The solid and the dashed line correspond to the stable and the metastable state, respectively, and the dotted line denotes the unstable solutions of the equation of equilibrium. Also shown are solutions obtained for $\mathcal{H}=0$

## Problem 5.13.

*How does within the Landau theory the magnetization at the critical point vary with the strength of magnetic field?*

At $T_c$ one has $g(M,T_c)=g(0,T_c)+bM^4/4-\mu_0HM/\rho$. The equilibrium magnetization is given by $(\partial g/\partial M)_T=bM^3-\mu_0H/\rho=0$ or

$$M(T_c,H)=\left(\frac{\mu_0H}{\rho b}\right)^{1/3}.$$

The critical exponent $\delta$ describing the dependence of the magnetization on the magnetic field strength at the critical temperature, $M(T_c, H) \propto H^{1/\delta}$, is thus equal to 3.

**Problem 5.14.**

*Nematic liquid crystals consist of elongated molecules which are orientationally ordered below a certain temperature $T_{NI}$, with a finite value of the corresponding order parameter. In the isotropic phase observed above $T_{NI}$, the orientational order is absent and the order parameter vanishes. The transition between the two phases is discontinuous. The Gibbs free energy of an inhomogeneous nematic per unit volume is given by*

$$g_N(T, S, \nabla S) = g_I(T) + \frac{1}{2}a(T - T^*)S^2 - \frac{1}{3}bS^3 + \frac{1}{4}cS^4 + \frac{3}{4}L_1(\nabla S)^2,$$

*where $S$ is the order parameter, $g_I(T)$ is the Gibbs free energy of the isotropic phase per unit volume; $a$, $b$, $c$, and $L_1$ are material constants, whereas $T^*$ is the so-called supercooling temperature. Calculate the nematic–isotropic phase transition temperature in a homogeneous sample! Calculate the maximum superheating temperature of the nematic phase! Determine the correlation length of orientational alignment in the isotropic phase at $T_{NI}$! Use $a = 0.13 \times 10^6$ J/m$^3$K, $b = 1.8 \times 10^6$ J/m$^3$, $c = 4.1 \times 10^6$ J/m$^3$, $L_1 = 1.1 \times 10^{-11}$ J/m, and $T^* = 307$ K! Hint: When calculating the correlation length, consider ordering at a wall that induces a given (small) value of the order parameter. In this case the $S^3$ and $S^4$ terms in the Gibbs free energy can be neglected.*

In a homogeneous sample, the nematic–isotropic phase transition is at a temperature $T_{NI}$. At this temperature, $g_N(T_{NI}) = g_I(T_{NI})$ so that

$$\frac{1}{2}a\left(T_{NI} - T^*\right)S_{NI}^2 - \frac{1}{3}bS_{NI}^3 + \frac{1}{4}cS_{NI}^4 = 0\,.$$

At the same time, the Gibbs free energy must have a minimum at $S_{NI}$:

$$\left(\frac{\partial g_N}{\partial S}\right)_T = a\left(T_{NI} - T^*\right)S_{NI} - bS_{NI}^2 + cS_{NI}^3 = 0\,.$$

From these two equations, we find that

$$S_{NI} = \frac{2b}{3c} = 0.29$$

and

$$T_{NI} = T^* + \frac{2b^2}{9ac} = 308.35\ \mathrm{K}\,.$$

At the maximum superheating temperature of the nematic phase $T^{**}$, the local minimum of $g_N$ at $S > 0$ just vanishes. By evaluating $\left(\partial^2 g_N/\partial S^2\right)_T = a\,(T - T^*) - 2bS + 3cS^2$ at the minimum at $S > 0$ we see that this derivative is positive at temperatures below

$$T^{**} = T^* + \frac{b^2}{4ac} = 308.52\ \mathrm{K}\,,$$

which thus represents the metastability limit of the nematic phase. Similarly, one can check that $T^*$ indeed represents the lowest supercooling temperature of the isotropic phase. At $S = 0$ which corresponds to the isotropic phase, the second derivative of the Gibbs free energy is $a(T - T^*)$ and is thus negative for $T < T^*$ so that below $T^*$, $g_N$ no longer exhibits a minimum at $S = 0$. Further, we find that the extremum at $S < 0$ corresponds to the metastable planar alignment for all $T < T^*$, and that it vanishes above $T^*$.

Now we follow the hint to determine the correlation length. We obtain the Euler–Lagrange equation that describes the spatial dependence of the order parameter close to an aligning wall:

$$\frac{\mathrm{d}^2 S}{\mathrm{d}z^2} = \xi^{-2} S\,.$$

Here $z$ is the distance from the wall and $\xi$ is the correlation length defined as

$$\xi = \sqrt{\frac{3L_1}{2a(T_{NI} - T^*)}} = 9.7\ \mathrm{nm}\,.$$

The meaning of $\xi$ is illustrated in Fig. 5.12: It gives the penetration depth of the orientational order introduced by the aligning wall.

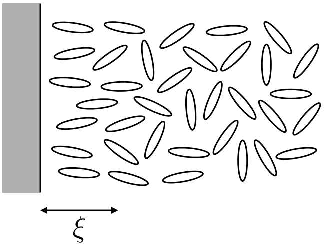

**Fig. 5.12** Nematic liquid crystal at an aligning wall: The order parameter decays exponentially with distance from the wall, and the correlation length $\xi$ gives the thickness of the partially ordered layer

**Problem 5.15.**

*For a generic discontinuous phase transition, the Gibbs free energy per unit mass can be modeled by*

$$g(T,\eta) = g_0(T) + \frac{1}{2}a(T-T^*)\eta^2 - \frac{1}{4}b\eta^4 + \frac{1}{6}c\eta^6,$$

*where* $\eta$ *is the order parameter,* $T$ *is temperature, and* $g_0(T)$ *is the free energy of the high-temperature phase per unit mass;* $a$, $b$, $c$, *and* $T^*$ *are positive constants. Calculate the latent heat of the transition!*

We first determine the critical temperature $T_c$ and the corresponding value of the order parameter in the low-temperature phase $\eta_c$. At the transition, the Gibbs free energy must have one minimum at $\eta = \eta_c$ and another one at $\eta = 0$, corresponding to the low- and the high-temperature phase, and their depths must be the same so that the phases coexist. These requirements lead to

$$a(T_c - T^*)\eta_c - b\eta_c^3 + c\eta_c^5 = 0$$

and

$$\frac{a}{2}(T_c - T^*)\eta_c^2 - \frac{b}{4}\eta_c^4 + \frac{c}{6}\eta_c^6 = 0$$

respectively, which can be solved to give $\eta_c = \pm\sqrt{3b/4c}$ and $T_c = T^* + 3b^2/16ac$. The latent heat $q = -T_c[s(\eta_c) - s(0)]$, where $s(\eta)$ is the entropy per unit mass:

$$s = -\frac{\mathrm{d}g}{\mathrm{d}T} = -\left(\frac{\partial g}{\partial T}\right)_\eta - \left(\frac{\partial g}{\partial \eta}\right)_T \frac{\mathrm{d}\eta}{\mathrm{d}T} = -\frac{\mathrm{d}g_0}{\mathrm{d}T} - \frac{a}{2}\eta^2.$$

In the last step, we took into account that in equilibrium $(\partial g/\partial\eta)_T = 0$. Finally, the latent heat is equal to $q = (3ab/8c)T_c$.

**Problem 5.16.**

*Calculate the latent heat of the normal–superconductor transition, if the temperature dependence of the critical magnetic field strength (above which the field can penetrate into the sample) is given by*

$$H_c = H_0\left[1 - (T/T_c)^2\right]!$$

*How does the difference of the heat capacities of the superconducting and normal phase at constant field strength depend on temperature?*

In the normal phase, the magnetization is very small and can be approximated by $M = 0$, whereas in the superconducting phase the sample behaves like a perfect diamagnet and $M = -H$. We denote the Gibbs free energy per unit mass of the normal phase by $g_N(T)$ and then integrate $\mathrm{d}g = -s\,\mathrm{d}T - (\mu_0 M/\rho)\,\mathrm{d}H$ from $H_c(T)$ where the free energies of the two phases are equal to $H < H_c(T)$. Thus, we obtain the Gibbs free energy per unit mass of the superconducting phase:

$$g_S(T, H) = g_N(T) + (\mu_0/2\rho)\left[H^2 - H_c(T)^2\right].$$

The latent heat is given by

$$\begin{aligned} q_{SN} &= T(s_N - s_S) = -T\left(\frac{\partial}{\partial T}(g_N - g_S)\right)_H = -\frac{\mu_0 T}{2\rho}\frac{\mathrm{d}H_c^2}{\mathrm{d}T} \\ &= \frac{2\mu_0 H_0^2}{\rho}\left(\frac{T}{T_c}\right)^2\left[1 - \left(\frac{T}{T_c}\right)^2\right] \end{aligned}$$

and vanishes at $T = 0$ and $T = T_c$, reaching a maximum at $T = T_c/\sqrt{2}$ (Fig. 5.13).

The heat capacity at constant field strength $c_H = T\ (\partial s/\partial T)_H$ so that

$$\begin{aligned} \Delta c_H &= c_H^S - c_H^N = T\left(\frac{\partial}{\partial T}(s_S - s_N)\right)_H = \frac{\mu_0 T}{2\rho}\frac{\mathrm{d}^2 H_c^2}{\mathrm{d}T^2} \\ &= \frac{2\mu_0 H_0^2}{\rho T_c}\frac{T}{T_c}\left[3\left(\frac{T}{T_c}\right)^2 - 1\right]. \end{aligned}$$

We see that $\Delta c_H$ is largest at $T_c$ where it is equal to $4\mu_0 H_0^2/\rho T_c$ (Fig. 5.13). At temperatures below $T_c/\sqrt{3}$ the heat capacity of the superconducting phase is smaller than that of the normal phase and vice versa at temperatures between $T_c/\sqrt{3}$ and $T_c$.

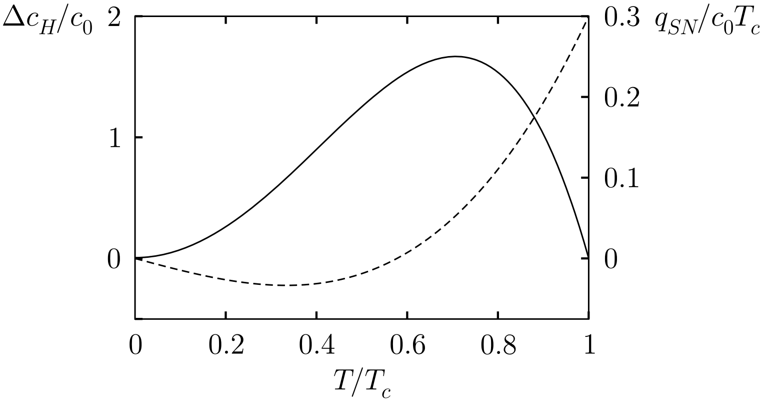

**Fig. 5.13** Difference of heat capacities of the superconducting and the normal phase (dashed line) and the latent heat of the normal–superconductor transition (solid line) plotted versus temperature; here $c_0 = 2\mu_0 H_0^2/\rho T_c$

**Problem 5.17.**

*The critical magnetic field strength for the normal–superconductor transition in niobium is given by* $H_c(T) = H_0\big[1 - (T/T_c)^2\big]$, *where* $H_0 = 1.58 \times 10^5$ A/m *and* $T_c = 9.26$ K. A 10 g *sample of niobium is heated in zero field from* 7 K to 11 K; *the amount of heat needed for the same process in a field of strength* $H_1$ is $10^{-3}$ J *less than in the zero-field case. Calculate* $H_1$*! The density of niobium is* $8570\ \mathrm{kg/m^3}$.

The amounts of heat needed to heat the sample of mass $m$ from $T_1$ to $T_2$ in zero field and in a field of strength $H_1$ (dashed lines in Fig. 5.14) are given by

$$Q_1 = m\left[\int_{T_1}^{T_c} c_H^S(T)\,\mathrm{d}T + q_{SN}(T_c) + \int_{T_c}^{T_2} c_H^N(T)\,\mathrm{d}T\right]$$

and

$$Q_2 = m\left[\int_{T_1}^{T'} c_H^S(T)\,\mathrm{d}T + q_{SN}(T') + \int_{T'}^{T_2} c_H^N(T)\,\mathrm{d}T\right],$$

respectively; here

$$T' = T_c\sqrt{1 - \frac{H_1}{H_0}}$$

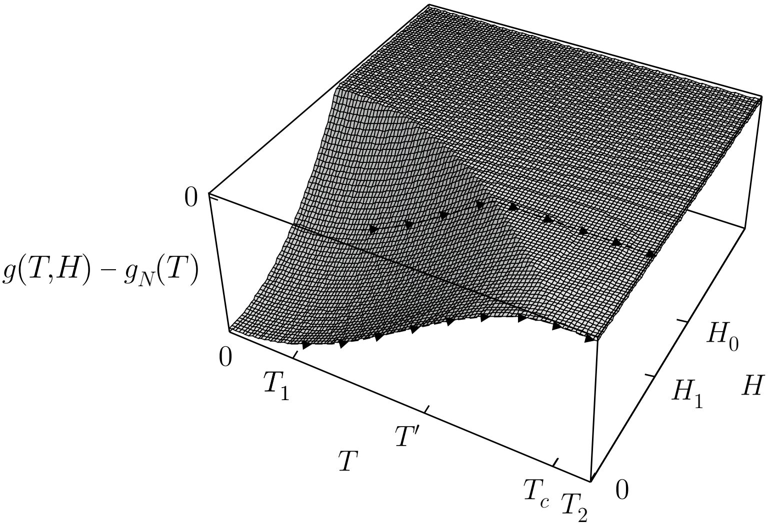

**Fig. 5.14** Gibbs free energy of niobium plotted relative to that of the normal phase represented by the horizontal plane. The dashed lines depict the two heating processes

denotes the phase transition temperature in a field of strength $H_1$, and the heat capacities $c_H^N$ and $c_H^S$ as well as of the latent heat $q_{SN}$ are borrowed from Problem 5.16. Note that $q_{SN}(T_c) = 0$: In zero field the transition is continuous. Finally, we find that $T' = 8.1$ K and

$$H_1 = \sqrt{\frac{2(Q_1 - Q_2)\rho}{\mu_0 m}} = 3.7 \times 10^4 \text{ A/m}\,.$$

**Problem 5.18.**

*The heat capacities of the superconducting and normal phase per unit volume can be approximated by*

$$c_S = aT^3$$

and

$$c_N = bT^3 + cT\,,$$

*respectively; here* $a = 10$ J/m$^3$K$^4$, $b = 8$ J/m$^3$K$^4$, *and* $c = 6$ J/m$^3$K$^2$. *Calculate the temperature of a thermally insulated superconducting sample, initially at* 1.5 K, *after the magnetic field strength is suddenly increased from* 0 to 7000 A/m*!*

We first construct the Gibbs free energies of the two phases, starting with their entropies per unit volume which read $s_S = \int_0^T (c_S/T)\,\mathrm{d}T = aT^3/3$ and $s_N = \int_0^T (c_N/T)\,\mathrm{d}T = bT^3/3 + cT$. Since at $H = 0$ the phase transition is continuous, at $T_c$ the entropies of the superconducting and the normal phase are equal: $s_S(T_c) = s_N(T_c)$. Thus

$$T_c = \sqrt{\frac{3c}{a-b}} = 3\text{ K}\,.$$

At $T_c$ the Gibbs free energies of the two phases per unit volume $g_S(T, H = 0) = -\int_0^T s_S\,\mathrm{d}T = -aT^4/12$ and $g_N(T) = -\int_0^T s_N\,\mathrm{d}T = -bT^4/12 - cT^2/2 + k$ must be equal too, and this gives $k = 3c^2/4(a - b)$. As the Gibbs free energy of the superconducting phase also includes a magnetic term with $M = -H$, we obtain

$$g_S(T, H) = -\frac{aT^4}{12} + \frac{\mu_0 H^2}{2\rho}$$

and

$$g_N(T) = -\frac{bT^4}{12} - \frac{cT^2}{2} + \frac{3c^2}{4(a-b)}\,;$$

like in Problem 5.16, we assumed that $M = 0$ in the normal phase. Now we turn to the critical magnetic field: At $H_c = H_c(T)$ the Gibbs free energies of the two phases are the same so that $H_c^2(T) = (2\rho/\mu_0)\left[(a - b)T^4/12 - cT^2/2 + 3c^2/4(a - b)\right]$ or

$$H_c(T) = H_0\left(1 - \mathcal{T}^2\right),$$

where $H_0 = T_c\sqrt{c\rho/2\mu_0}$ and $\mathcal{T} = T/T_c$. The latent heat of the phase transition is equal to $q_{SN} = T(s_N - s_S) = -(\mu_0 T/2\rho)\left(\mathrm{d}H_c^2/\mathrm{d}T\right)$ or

$$q_{SN} = cT_c^2\mathcal{T}^2\left(1 - \mathcal{T}^2\right).$$

After the magnetic field strength is suddenly increased to 7000 A/m, the superconducting sample is in a superheated state because the critical field strength at $T' = 1.5$ K is merely 3480 A/m. To convert this metastable state into the stable normal phase, the excess magnetic Gibbs free energy is partly utilized for the phase transition from the superconducting to the normal phase at $T'$ and partly for the heating of the normal phase from $T'$ to a higher temperature $T$. The latter part reads $\Delta g = (cT_c^2/4)\left[\mathcal{H}^2 - \left(1 + 3\mathcal{T}'^2\right)\left(1 - \mathcal{T}'^2\right)\right]$, where $\mathcal{H} = H/H_0$. The final state is thus determined by

$$\int_{T'}^{T} c_N \mathrm{d}T = \frac{cT_c^2}{4}\left(\frac{3b}{a-b}\mathcal{T}^4 + 2\mathcal{T}^2\right)_{\mathcal{T}'}^{\mathcal{T}}$$

or

$$\mathcal{H}^2 - \left(1 + 3\mathcal{T}'^2\right)\left(1 - \mathcal{T}'^2\right) = \frac{3b}{a-b}\mathcal{T}^4 + 2\mathcal{T}^2 - \frac{3b}{a-b}\mathcal{T}'^4 - 2\mathcal{T}'^2.$$

This is a quadratic equation for $\mathcal{T}^2$; we solve it and for $\mathcal{H} = 1.51$ and $\mathcal{T}' = 0.5$ we find that the final temperature in reduced units $\mathcal{T} = 0.595$ so that $T = 1.79$ K.

**Problem 5.19.**

*An ytterbium compound undergoes a phase transition from phase $\mathcal{F}$ with a temperature-independent magnetic susceptibility $\chi_0$ to phase $\mathcal{L}$ where the susceptibility at a temperature $T$ is given by the Curie law $C/T$. At a given temperature, phases $\mathcal{F}$ and $\mathcal{L}$ are stable below and above a critical magnetic field strength*

$$H_c(T) = H_0\sqrt{1 - \frac{T^2}{T_0^2}},$$

*respectively; here* $H_0 = 3\times 10^7$ A/m *and* $T_0 = 42$ K. *By how much do the heat capacities at constant field strength differ in the two phases coexisting at* 30 K*? The density of both phases is* 8400 kg/m$^3$, $\chi_0 = 0.005$, and $C = 1$ K. *—A thermostat at* 30 K *contains a* 100 g *sample of this compound, initially in the metastable $\mathcal{F}$ phase; magnetic field strength is* $4\times 10^7$ A/m. *How much heat does the sample exchange with the thermostat once equilibrium is established?*

The difference of heat capacities of two phases is related to the difference of the temperature derivatives of their entropies by

$$\Delta c_H = c_H^{\mathcal{L}} - c_H^{\mathcal{F}} = \frac{T}{m}\left[\left(\frac{\partial S_{\mathcal{L}}}{\partial T}\right)_H - \left(\frac{\partial S_{\mathcal{F}}}{\partial T}\right)_H\right] = \frac{T}{m}\left(\frac{\partial (Q_{\mathcal{LF}}/T)}{\partial T}\right)_H .$$

In the last step, we took into account that in coexistence, the difference of entropies is proportional to the latent heat of the transition $Q_{\mathcal{LF}} = T(S_{\mathcal{L}} - S_{\mathcal{F}})$. The latent heat can be obtained like in Problem 5.16 or by realizing that the Clausius–Clapeyron equation is nothing but a Maxwell relation applied to phase coexistence. For a magnetic system, this relation reads $(\partial S/\partial M)_T = -V\mu_0(\partial H/\partial T)_M$, or

$$\frac{S_{\mathcal{L}} - S_{\mathcal{F}}}{M_{\mathcal{L}} - M_{\mathcal{F}}} = \frac{Q_{\mathcal{LF}}}{TH_c(C/T - \chi_0)} = -V\mu_0\frac{\mathrm{d}H_c(T)}{\mathrm{d}T}.$$

By evaluating the derivative on the right-hand side, we see that the latent heat per unit mass is

$$\frac{Q_{\mathcal{LF}}}{m} = \frac{\mu_0 H_0^2(C - \chi_0 T)T}{\rho T_0^2} ,$$

where $\rho$ denotes the density of the compound, and thus

$$\Delta c_H = -\frac{T\mu_0\chi_0 H_0^2}{\rho T_0^2} = -11.4\ \text{J/kgK}.$$

(This approach can also be used in Problem 5.16.)

At 30 K, the critical magnetic field strength is $H_c = 2.1 \times 10^7$ A/m. Thus at $H = 4 \times 10^7$ A/m phase $\mathcal{F}$ is indeed metastable. The heat exchanged at constant $T$ and $H$ during the $\mathcal{F} \to \mathcal{L}$ transition is equal to the enthalpy difference $Q = \Delta(G + TS)$. As this transition is strongly irreversible, $Q < T\Delta S$ and the second law cannot be used to calculate $Q$. Instead we have to derive the Gibbs free energies $G_{\mathcal{L},\mathcal{F}}(T, H)$ and the entropies $S_{\mathcal{L},\mathcal{F}}(T, H)$ of both phases like in Problem 5.16. We start by recalling that at phase coexistence at a given temperature, $G_{\mathcal{F}}(T, H_c) = G_{\mathcal{L}}(T, H_c)$ and $Q_{\mathcal{LF}}/T = S_{\mathcal{L}}(T, H_c) - S_{\mathcal{F}}(T, H_c)$. Moreover,

$$\left(\frac{\partial G_{\mathcal{L},\mathcal{F}}}{\partial H}\right)_T = -\mu_0 V M_{\mathcal{L},\mathcal{F}} = \begin{cases} -V\mu_0\chi_0 H, & \text{phase } \mathcal{F} \\ -V\mu_0(C/T)H, & \text{phase } \mathcal{L} \end{cases} ,$$

and

$$\left(\frac{\partial S_{\mathcal{L},\mathcal{F}}}{\partial H}\right)_T = V\mu_0\left(\frac{\partial M_{\mathcal{L},\mathcal{F}}}{\partial T}\right)_H = \begin{cases} 0 & \text{phase } \mathcal{F} \\ -V\mu_0(C/T^2)H, & \text{phase } \mathcal{L} \end{cases} .$$

We can further write

$$G_{\mathcal{L},\mathcal{F}}(T,H) = G_{\mathcal{L},\mathcal{F}}(T,H_c) + \int_{H_c}^{H} \left(\frac{\mathrm{d}G_{\mathcal{L},\mathcal{F}}}{\mathrm{d}H}\right)_T \mathrm{d}H$$

and

$$S_{\mathcal{L},\mathcal{F}}(T,H) = S_{\mathcal{L},\mathcal{F}}(T,H_c) + \int_{H_c}^{H} \left(\frac{\mathrm{d}S_{\mathcal{L},\mathcal{F}}}{\mathrm{d}H}\right)_T \mathrm{d}H.$$

Imagine now a reversible path starting at $H > H_c$ in phase $\mathcal{F}$ whereby the sample reaches phase equilibrium at $H_c$ upon an isothermal decrease of the field strength, then undergoes a reversible $\mathcal{F} \to \mathcal{L}$ transition, and finally returns to the initial $H$ in phase $\mathcal{L}$ upon an isothermal increase of the field strength. This path can be used to calculate the exchanged heat given by the difference of enthalpies; note that all quantities involved—enthalpy, Gibbs free energy, and entropy—are functions of state. We find that the heat exchanged per unit mass is

$$\frac{Q}{m} = \frac{\mu_0}{\rho}\left(\frac{\chi_0}{2} - \frac{C}{T}\right)(H^2 - H_c^2) + \frac{Q_{\mathcal{L}\mathcal{F}}}{m}$$

so that 0.34 kJ of heat is emitted in the process.

**Problem 5.20.**

*Calculate the saturated electron current in a diode with a tungsten cathode heated to* 2000 °C*! The ionization energy is* 4.52 eV *and the surface area of the cathode is* 0.2 cm$^2$.

The entropy of the electron gas is equal to the entropy of the evaporated electrons or $\int_0^T (c_p/T)\,\mathrm{d}T + q_v/T = (R/M)\left[\ln(JT^{5/2}/p) + 5/2\right]$, where $J$ is the chemical constant. The first term on the left-hand side can be neglected because the heat capacity of electrons in tungsten is rather small. Now we are interested in $q_v(T)$: The Kirchhoff formula states that $\mathrm{d}q_v/\mathrm{d}T = \Delta\left[c_p + (\partial h/\partial p)_T\,(\mathrm{d}p/\mathrm{d}T)\right]$. By treating the evaporated electrons as an ideal gas, we have $(\partial h/\partial p)_T = 0$ and $c_p = 5R/2M$. Then $\mathrm{d}q_v/\mathrm{d}T = \Delta c_p \approx 5R/2M$ if as before the heat capacity of electrons in tungsten is neglected. Thus $q_v(T) = q_v(0) + 5RT/2M$ and since $Mq_v(0) = N_A E_i$, where $E_i$ is the work function, the pressure is given by

$$p = JT^{5/2}\exp\left(-\frac{E_i}{k_B T}\right).$$

Now assume that at a given accelerating voltage between the anode and the cathode, the electron flux density $j$ emitted from the cathode is the same as at zero voltage. From the kinetic theory of gases we have $j = n\langle v\rangle/4$, where $n = p/k_B T$ is the number density of electrons and $\langle v\rangle = \sqrt{8k_B T/\pi m_e}$ is their average speed. Then the current density is equal to $j_e = e_0 j$. By recalling that the chemical constant is given by $J = 2(2\pi m_e)^{3/2} k_B^{5/2} h^{-3}$, we find that the current

$$I = \frac{4\pi m_e e_0 k_B^2 T^2 A}{h^3} \exp\left(-\frac{E_i}{k_B T}\right) = 11.9\,\mathrm{mA}\,,$$

where $A$ is the surface area of the cathode. This result is known as Richardsons law, and the phenomenon itself is referred to as the thermionic emission.

**Problem 5.21.**

*A thermostat contains a sealed bottle with* 5 g of ice, 5 g *of liquid water, and* 5 g *of water vapor in coexistence at* 610 Pa *and* 0.01 °C. *What are the masses of ice, water, and vapor after* 1 kJ *of heat is supplied to the bottle? At this temperature, the heat of fusion is* 0.33 MJ/kg *and the heat of vaporization is* 2.47 MJ/kg. *The densities of ice and water are* 916 kg/m$^3$ *and* 1000 kg/m$^3$, *respectively, and the kilomolar mass of water is* 18 kg/kmol.

We assume that in the final state, the three phases are still in equilibrium so that pressure and temperature, which correspond to the triple point of water, remain unchanged. In the process, mass is conserved

$$m_s + m_l + m_v = 3m'\,,$$

where $m_s$, $m_l$, and $m_v$ denote the masses of ice, water, and vapor in the final state, respectively, whereas $m'$ is the initial mass of each of the phases. Also conserved is the total volume:

$$\frac{m'}{\rho_s} + \frac{m'}{\rho_l} + \frac{m'}{\rho_v} = \frac{m_s}{\rho_s} + \frac{m_l}{\rho_l} + \frac{m_v}{\rho_v}\,;$$

here $\rho_s$ and $\rho_l$ are the densities of ice and water, respectively, and the vapor density $\rho_v$ is given by the ideal gas equation of state: $\rho_v = pM/RT$. The third relation to be considered is enthalpy change:

$$Q = (m_v - m')(q_f + q_v) + (m_l - m')q_f\,.$$

Here $Q$ is the heat supplied, $q_f$ is the heat of fusion, and $q_v$ is the heat of vaporization. From these three conservation laws we obtain the masses of all the three phases in the final state: $m_s \approx 2$ g, $m_l \approx 8$ g, and $m_v \approx 5$ g. This result *a posteriori* justifies the introductory assumption.

# Chapter 6
# Mixtures

**Problem 6.1.**
*A ten-liter insulated vessel is divided into two equal compartments by a wall. The first compartment contains* $O_2$ *at* 5 bar and 80 °C, *whereas the second one contains* $CO_2$ *at* 2 bar *and* 50 °C. *The wall breaks so that the gases mix. Calculate the final temperature and pressure! Also calculate the changes of internal energy, enthalpy, and entropy! The heat capacities of* $O_2$ *and* $CO_2$ *at constant pressure are* 930 J/kgK *and* 914 J/kgK, *respectively, and the corresponding ratios of heat capacities* $c_p/c_V$ *are* 1.39 *and* 1.26, *respectively.*

Since mixing takes place at constant volume and the vessel is thermally insulated, the total internal energy of the system is conserved in the process. Therefore

$$\sum_i m_i c_V^i T_i' = \left(\sum_i m_i c_V^i\right) T\,,$$

where index $i$ refers to each of the two components. The masses $m_i$ are given by the ideal gas equation of state $m_i = p_i' V_i' M_i / R T_i'$ for each component prior to mixing; the primed quantities all correspond to the initial state. By using $R/M_i = c_p^i - c_V^i$ and $c_p^i / c_V^i = \kappa_i$, we find that the final temperature reads

$$T = \sum_i \frac{p_i' V_i'}{\kappa_i - 1} \Bigg/ \sum_i \frac{p_i' V_i'}{T_i'(\kappa_i - 1)} = 68.1\,^\circ\mathrm{C}\,.$$

The final pressure $p$ follows from $\sum_i (m_i/M_i) = \sum_i (p_i' V_i' / R T_i') = pV/RT$, where $V = \sum_i V_i'$, and is equal to

$$p = \frac{T}{V} \sum_i \frac{p_i' V_i'}{T_i'} = 3.47\ \mathrm{bar}\,.$$

G. Skačej and P. Ziherl, *Solved Problems in Thermodynamics and Statistical Physics*, https://doi.org/10.1007/978-3-030-27661-4_6

The change of enthalpy is $\Delta H = \sum_i m_i c_p^i (T - T_i') = -28.8$ J; the change of entropy is $\Delta S = \sum_i \left[m_i c_p^i \ln\left(T/T_i'\right) - (m_i R/M_i)\ln\left(p_i/p_i'\right)\right] = 7.1$ J/K, where $p_i$ denotes the partial pressure of component $i$ in the final state.

**Problem 6.2.**
*Calculate the osmotic pressure of a* 0.2% *solution of sugar* $C_{12}H_{22}O_{11}$ *at* 20 °C*! Determine the corresponding shifts of the boiling and melting points with respect to pure water!*

We denote the solvent (water) by $A$ and the solute (sugar) by $B$, and consider a U tube with a semipermeable membrane (Fig. 6.1). One compartment contains pure water with a chemical potential $\mu_A^\circ(T, p)$, whereas the other one contains the sugar solution where the chemical potential of the solvent depends on the mole fraction of the solute $\widetilde{x}_B = 1 - \widetilde{x}_A$ and is equal to $\mu_A(T, p + \Delta p, \widetilde{x}_A)$. In equilibrium, the pressure difference across the membrane is equal to the osmotic pressure $\Delta p$, the chemical potentials of the solvent on both sides of the membrane being equal. In a dilute (ideal) solution we have

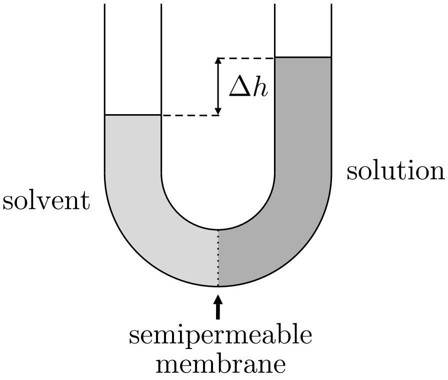

**Fig. 6.1** U tube containing a semipermeable membrane used in measurements of osmotic pressure

$$\begin{aligned}\mu_A(T, p + \Delta p, \widetilde{x}_A) &= \mu_A^\circ(T, p + \Delta p) + \frac{RT}{M_A}\ln\widetilde{x}_A \\ &= \mu_A^\circ(T, p) + \frac{\Delta p}{\rho_A} + \frac{RT}{M_A}\ln\widetilde{x}_A\,;\end{aligned}$$

here $M_i$ ($i = A, B$) stands for the kilomolar mass of each component in the solution. Upon expanding the logarithm for $\widetilde{x}_A \approx 1$ (which corresponds to $\widetilde{x}_B \ll 1$), we can express the osmotic pressure from $\mu_A^\circ(T, p) = \mu_A(T, p + \Delta p, \widetilde{x}_A)$ to find

$$\Delta p = \frac{\rho_A RT x_B}{M_B},$$

where $x_B \approx \widetilde{x}_B M_B/M_A$ is the mass fraction of sugar. For $\rho_A = 10^3$ kg/m$^3$, $T = 20\,°\mathrm{C}$, $x_B = 0.002$, and $M_B = 342$ kg/kmol, we have $\Delta p = 1.42 \times 10^4$ Pa.

We now focus on the boiling-point elevation. At the boiling temperature $T$ and pressure $p$, the pure solvent ($l$) must be in equilibrium with its vapor ($v$) and their chemical potentials must be the same:

$$\mu_A^{l\circ}(T,p) = \mu_A^v(T,p)\,.$$

Once the solute (which is assumed not to evaporate) is added to the solvent, the chemical equilibrium at constant pressure shifts to $T + \Delta T$. This is accompanied by a change in both chemical potentials which, however, remain equal:

$$\mu_A^l(T+\Delta T, p, \widetilde{x}_A) = \mu_A^v(T+\Delta T, p)\,.$$

At constant pressure, $\Delta\mu_i = -s_i\,\Delta T$ $(i = A, B)$, where $s_i$ is the specific entropy of a given phase. We expand this equation for small $\Delta T$ and $\widetilde{x}_B = 1 - \widetilde{x}_A \ll 1$, and note that the heat of vaporization of the solvent is given by $q_v = T(s_A^v - s_A^l)$. This leads to

$$\frac{\Delta T}{T} = \frac{RT x_B}{M_B q_v}\,.$$

For $q_i = 2.26$ MJ/kg and $T = 373$ K one obtains $\Delta T = 0.003$ K. A similar expression can be derived for the melting point depression; $q_f = 336$ kJ/kg gives $\Delta T = -0.011$ K. Note that the signs of the boiling-point elevation and the melting-point depression are opposite: In the former case, the presence of the solute decreases the chemical potential of the low-temperature phase, whereas in the latter case it decreases the chemical potential of the high-temperature phase.

**Problem 6.3.**
*Determine the equilibrium composition of a gaseous mixture containing three isomers of pentane (n-pentane, isopentane, and neopentane) at* 1 bar *and* 298 K*! The corresponding standard Gibbs free energy of formation for the three isomers in the reaction* $5\mathrm{C} + 6\mathrm{H}_2 \to \mathrm{C}_5\mathrm{H}_{12}$ *are* 40.195 kJ/mol, 34.415 kJ/mol, *and* 37.640 kJ/mol, *respectively.*

The dynamical equilibrium between the isomers is represented by the reaction $\nu_A A + \nu_B B \rightleftharpoons \nu_C C$, where $A$, $B$, and $C$ denote $n$-pentane, isopentane, and neopentane, respectively. In equilibrium at constant pressure and temperature the total Gibbs free energy is minimal, which implies that for an attempted change in composition d$n$

$$\mathrm{d}G = -\nu_A M_A \mu_A\,\mathrm{d}n - \nu_B M_B \mu_B\,\mathrm{d}n + \nu_C M_C \mu_C\,\mathrm{d}n = 0\,.$$

Here $\nu_i M_i \mathrm{d}n$ are the masses of the synthesized/decomposed component $i = A, B, C$ ($\nu_i \mathrm{d}n$ being the change of amount in moles), $M_i$ are the corresponding molar masses, and $\mu_i$ are the corresponding chemical potentials. Therefore

$$\nu_A M_A \mu_A + \nu_B M_B \mu_B = \nu_C M_C \mu_C \,.$$

For an ideal gas with a partial pressure $p_i$ one has

$$\mu_i(T, p_i) = \mu_i^\circ(T, p) + \frac{RT}{M_i} \ln \frac{p_i}{p} \,,$$

where $\mu_i^\circ(T, p)$ refers to the gas of pure component $i$ at a pressure $p$ and temperature $T$. Upon introducing the mole fraction

$$\widetilde{x}_i = \frac{m_i/M_i}{\sum_i (m_i/M_i)} = \frac{p_i}{p} \,,$$

one obtains

$$RT \ln \frac{\widetilde{x}_A^{\nu_A} \widetilde{x}_B^{\nu_B}}{\widetilde{x}_C^{\nu_C}} = \left(\nu_C M_C \mu_C^\circ - \nu_B M_B \mu_B^\circ - \nu_A M_A \mu_A^\circ\right)_{Tp} \,.$$

The expression in the brackets corresponds to the change of the Gibbs free energy in a hypothetical reaction where all reactants are converted to products. Now consider the equilibrium $n\mathrm{C_5H_{12}} \rightleftharpoons$ iso$\mathrm{C_5H_{12}}$. We insert $\nu_A = 1$, $\nu_B = -1$, and $\nu_C = 0$ into the above expression, and the change of the Gibbs free energy is $\Delta G_B - \Delta G_A = -5.78$ kJ/mol where $\Delta G_i$ ($i = A, B, C$) is the standard Gibbs free energy of formation of isomer $i$. We obtain

$$\frac{\widetilde{x}_A}{\widetilde{x}_B} = \exp\left(\frac{\Delta G_B - \Delta G_A}{RT}\right) = 0.097 \,.$$

For the equilibrium $n\mathrm{C_5H_{12}} \rightleftharpoons$ neo$\mathrm{C_5H_{12}}$ one writes $\nu_A = 1$, $\nu_B = 0$, $\nu_C = 1$, and $\Delta G_C - \Delta G_A = -2.55$ kJ/mol, yielding

$$\frac{\widetilde{x}_A}{\widetilde{x}_C} = \exp\left(\frac{\Delta G_C - \Delta G_A}{RT}\right) = 0.356 \,.$$

As $\widetilde{x}_A + \widetilde{x}_B + \widetilde{x}_C = 1$, we find that $\widetilde{x}_A = 0.071$ ($n$-pentane), $\widetilde{x}_B = 0.730$ (isopentane), and $\widetilde{x}_C = 0.199$ (neopentane). The mixture is dominated by isopentane, which has the smallest standard Gibbs free energy of formation of all three isomers.

**Problem 6.4.**
*The solar photosphere can be represented by an ideal-gas mixture of electrons, protons, and atomic hydrogen. The ionization energy of hydrogen is equal to* 13.6 eV. *What is the dependence of the concentration of atomic hydrogen on temperature?*

The dynamic equilibrium in the photosphere is represented by the reaction $\mathrm{H} \rightleftharpoons \mathrm{H}^+ + \mathrm{e}^-$ with

$$\mu_\mathrm{H}\mathrm{M}_\mathrm{H} = \mu_{\mathrm{H}^+}\mathrm{M}_{\mathrm{H}^+} + \mu_{\mathrm{e}^-}\mathrm{M}_{\mathrm{e}^-} .$$

In an ideal gas, the chemical potential of component $i$ reads $\mu_i(T, p_i) = \mu_i^\circ(T, p) + (R/M_i)T \ln(p_i/p)$, where $p_i$ is the partial pressure and $\mu_i^\circ(T, p)$ is the chemical potential of a pure component at a total pressure $p$. It follows that

$$\mu_\mathrm{H}^\circ M_\mathrm{H} - \mu_{\mathrm{H}^+}^\circ M_{\mathrm{H}^+} - \mu_{\mathrm{e}^-}^\circ M_{\mathrm{e}^-} = RT \ln\left(\frac{p_{\mathrm{H}^+} p_{\mathrm{e}^-}}{p_\mathrm{H} p}\right).$$

Each of the chemical potentials $\mu_i^\circ(T, p)$ can be recast as $\mu_i^\circ(T, p) = u_i + p/\rho_i - Ts_i$, where $\rho_i$, $u_i$, and $s_i$ are the mass densities of matter, internal energy, and entropy of the pure components. A part of the left-hand side of the above equation represents the ionization energy

$$E_i = \frac{-u_\mathrm{H} M_\mathrm{H} + u_{\mathrm{H}^+} M_{\mathrm{H}^+} + u_{\mathrm{e}^-} M_{\mathrm{e}^-}}{N_A},$$

where $N_A = 6 \times 10^{26}\ \mathrm{kmol}^{-1}$ is the Avogadro number. By using the ideal gas equation of state $pM_i/\rho_i = RT$ and by substituting $s_i$ by $(R/M_i)\left[\ln(J_i T^{5/2}/p) + 5/2\right]$, where $J_i$ is the chemical constant of component $i$, we obtain

$$\frac{p_{\mathrm{H}^+} p_{\mathrm{e}^-}}{p_\mathrm{H}} = \frac{J_{\mathrm{H}^+} J_{\mathrm{e}^-}}{J_\mathrm{H}} T^{5/2} \exp\left(-\frac{N_A E_i}{RT} + \frac{3}{2}\right).$$

We need to evaluate the degree of dissociation of atomic hydrogen quantified by

$$\alpha = \frac{p_\mathrm{H}}{p_\mathrm{H} + p_{\mathrm{H}^+} + p_{\mathrm{e}^-}},$$

since particle number density is proportional to the partial pressure $p_i$. From $\mathrm{H} \rightleftharpoons \mathrm{H}^+ + \mathrm{e}^-$ it follows that $p_{\mathrm{H}^+} = p_{\mathrm{e}^-}$; evidently $p = p_\mathrm{H} + p_{\mathrm{H}^+} + p_{\mathrm{e}^-}$. We find that

$$\frac{(1-\alpha)^2}{\alpha} \propto \frac{T^{5/2}}{p} \exp\left(-\frac{N_A E_i}{RT}\right)$$

and finally compute $\alpha = \alpha(T)$ numerically; the result is shown in Fig. 6.2. Limiting cases: For $T \to \infty$ we have $\alpha = 0$ (all hydrogen is dissociated), whereas for $T \to 0$ $\alpha \to 1$ (all hydrogen is in the atomic form).

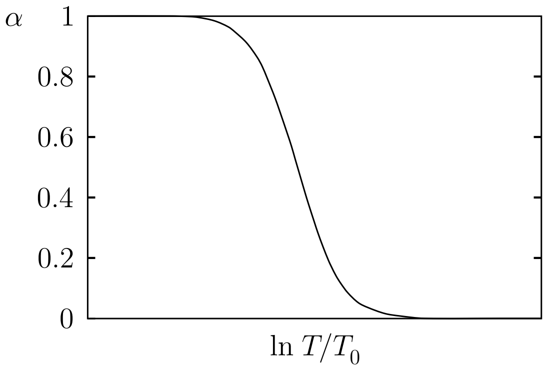

**Fig. 6.2** Degree of dissociation of atomic hydrogen in the solar photosphere shown schematically as a function of temperature; $T_0 = N_A E_i/R$ is the characteristic temperature

## Problem 6.5.

*The dissociation of molecular sodium* $\mathrm{Na}_2^{(g)} \rightleftharpoons 2\,\mathrm{Na}^{(g)}$ *is an equilibrium reaction where both reactant and product are gaseous. At* 1000 K, *the partial pressure of* $\mathrm{Na}_2$ *corresponds to one quarter of the total pressure. How does this partial pressure change after the mixture is heated by* 10 K *at constant pressure? The dissociation energy of* $\mathrm{Na}_2$ *is* 70.4 MJ/kmol.

From the balance of the Gibbs free energy in dynamic equilibrium we obtain a relation between the chemical potentials of $\mathrm{Na}_2$ and Na: $\mu_{\mathrm{Na}_2}(T, p_{\mathrm{Na}_2})M_{\mathrm{Na}_2} = 2\mu_{\mathrm{Na}}(T, p_{\mathrm{Na}})M_{\mathrm{Na}}$. If spelled out with respect to the reference pressure $p = p_{\mathrm{Na}_2} + p_{\mathrm{Na}}$, this relation reads

$$\mu^{\circ}_{\mathrm{Na}_2}(T, p)M_{\mathrm{Na}_2} + RT\ln\frac{p_{\mathrm{Na}_2}}{p} = 2\mu^{\circ}_{\mathrm{Na}}(T, p)M_{\mathrm{Na}} + 2RT\ln\frac{p_{\mathrm{Na}}}{p}\,;$$

the quantities denoted by ° again refer to pure substances. After introducing $x = p_{\mathrm{Na}}/p$ we have

$$\frac{\mu^{\circ}_{\mathrm{Na}_2}}{T}\frac{M_{\mathrm{Na}_2}}{R} - 2\frac{\mu^{\circ}_{\mathrm{Na}}}{T}\frac{M_{\mathrm{Na}}}{R} = \ln\frac{x^2}{1-x} \equiv \alpha(T)\,.$$

We now calculate the change of concentration $x$ after temperature is increased, and to this end we examine the temperature dependence of $\alpha(T)$. We find that $\left(\partial(\mu/T)/\partial T\right)_p = -h/T^2$, where $h$ stands for the enthalpy per unit mass. Thus

$$RT^2\left(\frac{\partial\alpha}{\partial T}\right)_p = -h^{\circ}_{\mathrm{Na}_2}M_{\mathrm{Na}_2} + 2h^{\circ}_{\mathrm{Na}}M_{\mathrm{Na}} = \Delta H_r\,.$$

The right-hand side represents the enthalpy of reaction. By taking into account the ideal gas equation of state, we can express it in terms of the dissociation energy $\Delta U_r = \Delta H_r - RT$ which gives $(\partial\alpha/\partial T)_p = 9.5 \times 10^{-3}\,\mathrm{K}^{-1}$. In the initial state we have $\alpha(T) = 0.81$, and in the final state $\alpha(T + \Delta T) \approx \alpha(T) + (\partial\alpha/\partial T)_p\,\Delta T = 0.905$. Here we assumed that $\Delta U_r \neq \Delta U_r(T)$. The final concentration of atomic sodium $x_f$ is found by solving the quadratic equation

$$x_f^2 + \exp\bigl(\alpha(T + \Delta T)\bigr)(x_f - 1) = 0$$

and the physically relevant solution is $x_f = 0.764$ so that the partial pressure of $\mathrm{Na_2}$ is $(1 - x_f)p = 0.236\,p$.

**Problem 6.6.**
*A vessel contains water and ether, which do not mix. A non-evaporating amphiphilic colorant soluble in both fractions is added; as a consequence, the boiling point of the water fraction increases by* 0.01 K. *Calculate the shift of boiling point of the ether fraction given that both solutions are ideal and in equilibrium! The kilomolar masses of colorant, ether, and water are equal to* 340 kg/kmol, 74 kg/kmol, *and* 18 kg/kmol, *respectively. The boiling points of water and ether are* 100 °C *and* 34.6 °C, *respectively; the corresponding latent heats are* 2.26 MJ/kg *and* 0.35 MJ/kg, *respectively.*

We denote the boiling point of component $i$ by $T_i$, its shift after the colorant is added by $\Delta T_i$, the kilomolar mass by $M_i$, and the latent heat of vaporization by $q_i$; in colorant, ether, and water, $i = c, e$, and $w$, respectively. In equilibrium, the chemical potentials of the colorant in the water and ether fractions, $\mu(\widetilde{x}_w)$ and $\mu(\widetilde{x}_e)$, are equal; $\widetilde{x}_w$ and $\widetilde{x}_e$ stand for the corresponding mole fractions of the colorant. For ideal solutions we have $\mu(\widetilde{x}_w) = \mu^\circ + (RT/M_c)\ln\widetilde{x}_w$ and $\mu(\widetilde{x}_e) = \mu^\circ + (RT/M_c)\ln\widetilde{x}_e$; $\mu^\circ$ denotes the chemical potential of pure colorant. Then $\mu(\widetilde{x}_w) = \mu(\widetilde{x}_e)$ leads to $\widetilde{x}_w = \widetilde{x}_e$ or $x_w M_w \approx x_e M_e$ for dilute solutions; $x_w$ and $x_e$ are the corresponding mass fractions. From the shift of the boiling point $\Delta T_w$ we now calculate the mass fractions of the colorant in both water and ether fractions: $x_w = M_c q_w\,\Delta T_w/RT_w^2 = 6.6 \times 10^{-3}$ and $x_e = x_w M_w/M_e = 1.6 \times 10^{-3}$. Thus the boiling point of the ether fraction increases by

$$\Delta T_e = \frac{RT_e^2 x_e}{M_c q_e} = 0.0107\,\mathrm{K}\,.$$

**Problem 6.7.**
*Consider the system from Problem 6.6, now kept at* 20 °C. *From a sample of the ether fraction containing the colorant, one finds that its vapor pressure is lower than in pure ether by* 4.3 mbar; *in pure ether it is* 586 mbar. *Calculate the mass fraction of the colorant in the ether fraction! Calculate the decrease of the vapor pressure of water above the water fraction, assuming that the colorant does not evaporate!*

*The saturated vapor pressure of water is* 23.37 mbar, *and the densities of ether and water are* 713 kg/m$^3$ *and* 1000 kg/m$^3$, *respectively.*

Like in Problem 6.6 we first conclude that in equilibrium the mole fractions of the colorant in the two solutions are equal, $\widetilde{x}_e = \widetilde{x}_w \equiv \widetilde{x}$. Next, we determine the relation between the colorant concentration and the decrease of the solvent (e.g., ether) vapor pressure. When pure liquid ether is in equilibrium with its vapor, their chemical potentials $\mu_e^{\circ l}(T, p)$ and $\mu_e^g(T, p)$, respectively, are equal. This also holds after the colorant is added, but the equilibrium is accompanied by a pressure drop $\Delta p$: $\mu_e^l(T, p - \Delta p, 1 - \widetilde{x}) = \mu_e^g(T, p - \Delta p)$, where $1 - \widetilde{x}$ is the molar fraction of ether in solution. This can be rewritten as

$$\mu_e^{\circ l}(T, p) + \int_p^{p-\Delta p} \frac{\mathrm{d}p}{\rho_e^l} + \frac{RT}{M_e} \ln(1 - \widetilde{x}) = \mu_e^g(T, p) + \int_p^{p-\Delta p} \frac{\mathrm{d}p}{\rho_e^g},$$

where $\rho_e^l$ and $\rho_e^g = pM_e/RT$ are the densities of liquid and gaseous ether, respectively. By assuming that in the pressure range considered $\rho_e^l$ barely changes, we obtain

$$-\frac{\Delta p}{\rho_e^l} + \frac{RT}{M_e} \ln(1 - \widetilde{x}) = \frac{RT}{M_e} \ln\left(1 - \frac{\Delta p}{p}\right).$$

Since $\rho_e^g \ll \rho_e^l$, the first term on the left-hand side is negligible and hence the relative decrease of vapor pressure in the ether fraction is simply given by $\Delta p/p = \widetilde{x} = 7.3 \times 10^{-3}$. Thus the mass fraction of the colorant in the ether solution is

$$x_c^e = \frac{1}{1 + (M_w/M_c)(\widetilde{x}^{-1} - 1)} = 0.122.$$

(The above result $\Delta p/p = \widetilde{x}$ is closely related to Raoult's law stating that, in an ideal mixture, the partial vapor pressure of any of its components is equal to the vapor pressure of the pure component multiplied by its mole fraction.)

Because $\widetilde{x}_e = \widetilde{x}_w = \widetilde{x}$, the relative decrease of the vapor pressure of the water fraction is the same as that of the ether fraction, i.e., $7.3 \times 10^{-3}$, so that the absolute pressure decrease is 0.17 mbar. (Note that at 20 °C the vapor pressures of ether and water differ, leading to different $\Delta p$s.)

**Problem 6.8.**
*A membrane permeable only to water divides a vessel into two compartments. The first compartment contains a* 0.5% *water solution of glucose, whereas the second one contains a* 0.8% *water solution of sucrose. Calculate the pressure difference across the membrane in equilibrium at* 90 °C*! The kilomolar masses of water, glucose, and sucrose are* 18 kg/kmol, 180 kg/kmol, *and* 342 kg/kmol, *respectively. Assume that the solutions are ideal and that water is incompressible, its density*

*being* 1000 $\mathrm{kg/m^3}$. *How does the result change if both solution concentrations are increased to* 100 *times their initial value?*

We label the compartments containing containing the glucose and the sucrose solution by 1 and 2, respectively, and we denote water, glucose, and sucrose by A, B, and C, respectively. In equilibrium, the chemical potentials of water in the two compartments are equal, i.e., $\mu_A\left(T, p_1, \widetilde{x}_A^{(1)}\right) = \mu_A\left(T, p_2, \widetilde{x}_A^{(2)}\right)$, where $\widetilde{x}_A^{(1)}$ and $\widetilde{x}_A^{(2)}$ are the corresponding mole fractions of water. The chemical potentials are related to that of pure water, $\mu_A^\circ(T, p_0)$, at a reference pressure $p_0$ by

$$\mu_A^\circ(T, p_0) + \frac{p_1 - p_0}{\rho_A} + \frac{RT}{M_A}\ln\widetilde{x}_A^{(1)} =$$
$$\mu_A^\circ(T, p_0) + \frac{p_2 - p_0}{\rho_A} + \frac{RT}{M_A}\ln\widetilde{x}_A^{(2)} ,$$

which gives the pressure difference across the membrane:

$$p_2 - p_1 = \frac{\rho_A RT}{M_A}\left[\ln\widetilde{x}_A^{(1)} - \ln\widetilde{x}_A^{(2)}\right] .$$

This result can be interpreted as the difference of osmotic pressures of the two solutions, each of them measured against pure water. The mole fractions of water are given by $\widetilde{x}_A^{(1)} = 1 - \widetilde{x}_B$ and $\widetilde{x}_A^{(2)} = 1 - \widetilde{x}_C$, where

$$\widetilde{x}_{B,C} = \left[\frac{M_{B,C}}{M_A}\left(\frac{1}{x_{B,C}} - 1\right) + 1\right]^{-1} ;$$

$x_B$ and $x_C$ are the mass fractions of the two solutes. Finally we find that the pressure difference is $-13$ kPa. After the concentrations of both solutes are increased 100 times, the pressure difference is 16 MPa. Note that apart from the evident increase in magnitude, the pressure difference also differs in sign compared to that at the lower concentrations.

### Problem 6.9.

*In humid air containing saturated water vapor at* 300 K, *droplets condense around tiny charged particulate seeds. If the droplets contain* 1% *glucose solution, their equilibrium radius is* 1 $\mu$m. *Calculate the equilibrium radius of droplets of pure water! The surface tension, relative permittivity, and density of water are* 0.073 N/m, 81, *and* $10^3$ $\mathrm{kg/m^3}$, *respectively, and the kilomolar mass of glucose is* 342 kg/kmol.

Water vapor at the saturated vapor pressure $p_s$ is in equilibrium with liquid water at the atmospheric pressure $p$:

$$\mu_v(T, p_s) = \mu_l^\circ(T, p) ,$$

where $\mu_v(T, p_s)$ and $\mu_l^\circ(T, p)$ are the chemical potentials of water vapor and liquid water, respectively. Simultaneously, it is also in equilibrium with the pure-water droplets and the glucose-solution droplets, where the chemical potential of water is $\mu_l^\circ(T, p')$ and $\mu_l(T, p'', x)$, respectively; $x$ stands for the mass fraction of glucose.

Hence

$$\mu_l(T, p'', x) = \mu_l^\circ(T, p) + \frac{p'' - p}{\rho} - \frac{RTx}{M} = \mu_v(T, p_s)\,,$$

which gives $p'' - p = \rho RTx/M$; here $M$ denotes the kilomolar mass of sugar and $\rho$ the density of water. The pressure difference $p'' - p$ is due to both surface tension and electrostatic charge. The electrostatic pressure is calculated like in Problem 4.15 using the principle of virtual work. One must be careful when writing the change of density of electrostatic energy upon an infinitesimal expansion of the droplet: The electric charge of the seed $e$ is located in the center of the droplet and is surrounded by water of relative permittivity of $\epsilon = 81$ so that

$$p'' - p = \frac{2\gamma}{r''} - \frac{e^2}{32\pi^2\epsilon_0 r''^4}\left(1 - \frac{1}{\epsilon}\right) = \frac{\rho RTx}{M}\,,$$

where $\gamma$ stands for the surface tension of water and $r'' = 1\ \mu$m is the radius of the droplet. From here we can calculate the magnitude of the electric charge of the seed, which is $e = 1.44 \times 10^{-14}$ As. For pure-water droplets of diameter $r'$ we have

$$\mu_l^\circ(T, p') = \mu_l^\circ(T, p) + \frac{p' - p}{\rho} = \mu_v(T, p_s)\,,$$

which implies that $p = p'$ and

$$p' - p = \frac{2\gamma}{r'} - \frac{e^2}{32\pi^2\epsilon_0 r'^4}\left(1 - \frac{1}{\epsilon}\right) = 0\,.$$

Finally we have $r' = \sqrt[3]{e^2(\epsilon - 1)/64\pi^2\gamma\epsilon\epsilon_0} = 0.8\ \mu$m.

**Problem 6.10.**

*Interpret the boiling-point diagram of an ideal binary fluid solution, e.g., a mixture of fluid nitrogen and oxygen! (The diagram also applies to ideal alloys like the copper–nickel alloy.) Derive the expression for the dew-point curve and the bubble-point curve!*

We denote the two components of the mixture by $A$ and $B$, and consider the mixture at a constant pressure where the phase diagram depends on temperature and on composition represented by the concentration of one of the components, say $\widetilde{x}_B$ (Fig. 6.3). The phase diagram is divided into three regions: The liquid and the vapor region at low and high temperatures, respectively, are separated by the two-phase region where liquid and vapor mixtures coexist. In the two-phase region, the concentrations of the two phases are different from each other, and they depend only on temperature and not on the overall concentration. The state of the vapor–liquid mixture in the two-phase region is also described by the mass fractions of the vapor and the liquid phase—when cutting across the two-phase region along a horizontal constant-temperature line from the dew-point curve to the bubble-point curve, the fractions of the vapor and the liquid phase change from 100% to 0 and from 0 to 100%, respectively, whereas the concentrations of the vapor and the liquid phase themselves remain constant.

Upon heating at constant concentration $\widetilde{x}_B$, the initially liquid-phase binary mixture transforms as indicated by the dashed path in the diagram in Fig. 6.3. In the liquid region (line MN), the temperature of the mixture increases upon heating just like in a pure substance. At the bubble-point curve, the mixture consists of the vapor phase with concentration N’ and of the liquid phase with concentration N, with the mass fraction of the vapor phase being negligible compared to that of the liquid phase. Upon further heating, the temperature of the mixture increases while the vapor and the liquid phase both get richer and richer in component $B$ (points O’ and O); at the same time, the mass fraction of the vapor phase increases. At point P’ the concentration of the vapor phase is equal to the initial concentration of the liquid phase, the mass fraction of the liquid phase of concentration given by point P being infinitesimally small. Along line P’R the vapor phase behaves like a pure substance.

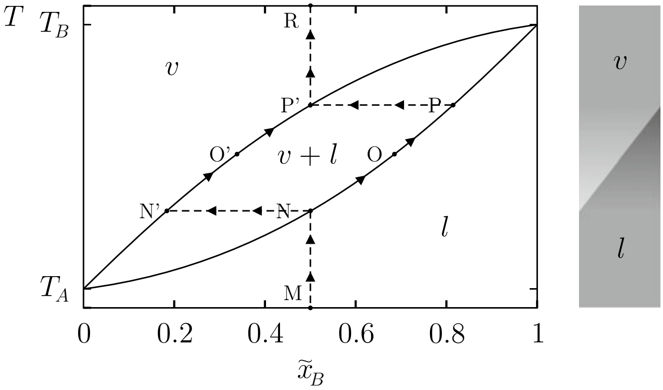

**Fig. 6.3** Boiling-point diagram of an ideal binary fluid mixture where the two components are perfectly miscible. The state of the mixture is illustrated by the diagram on the right, consisting of the vapor ($v$) and the liquid ($l$) phase. The shade of gray indicates the concentration of component $B$. In the two-phase region the mixture consists of the $B$-poor vapor phase and of the $B$-rich liquid phase. With increasing temperature, the mass fraction of the vapor phase increases whereas that of the liquid phase decreases. This is further elaborated in Problem 6.11

The behavior of the mixture in the two-phase region is exploited in distillation, where the $B$-poor vapor phase and the $B$-rich liquid phase are physically separated, e.g., by pumping the vapor phase. After multiple cycles of pumping, condensation, and reevaporation of the vapor mixture, one can significantly reduce the concentration of component $B$; however, after every cycle the mass of the concentrate rich in component $A$ is reduced too.

We now analyze the characteristic shape of the two-phase region. In the entire concentration range, the chemical potential of each component of the ideal mixture $\mu_i$ ($i = A, B$) is given by $\mu_i = \mu_i^\circ + (RT/M_i)\ln\widetilde{x}_i$, where $\mu_i^\circ$ refers to a pure component $i$ and $\widetilde{x}_i$ denotes the mole fraction of the component. In the following, indices $v$ and $l$ correspond to vapor and liquid, respectively. We consider chemical equilibrium along an isotherm cutting across the two-phase region from the dew-point curve to the bubble-point curve. Along the isotherm we have $\mu_i^v\big(\widetilde{x}_i^v\big) = \mu_i^l\big(\widetilde{x}_i^l\big)$ or

$$\mu_i^{v\circ} + \frac{RT}{M_i}\ln\widetilde{x}_i^v = \mu_i^{l\circ} + \frac{RT}{M_i}\ln\widetilde{x}_i^l\,.$$

Together with the constraints $\widetilde{x}_A^l + \widetilde{x}_B^l = 1$ with $\widetilde{x}_A^v + \widetilde{x}_B^v = 1$, this equation determines the mole fractions of component $i$ at the dew-point curve and the bubble-point curve $\widetilde{x}_i^v(T)$ and $\widetilde{x}_i^l(T)$, respectively. We find that

$$\widetilde{x}_B^v(T) = \frac{1 - \exp\big(-\lambda_A(T)\big)}{\exp\big(-\lambda_B(T)\big) - \exp\big(-\lambda_A(T)\big)}$$

and

$$\widetilde{x}_B^l(T) = \frac{\exp\big(\lambda_A(T)\big) - 1}{\exp\big(\lambda_A(T)\big) - \exp\big(\lambda_B(T)\big)}\,,$$

where $\lambda_i(T) = \big(\mu_i^{l\circ} - \mu_i^{v\circ}\big)M_i/RT$; analogous expressions are obtained for $\widetilde{x}_A^v(T)$ and $\widetilde{x}_A^l(T)$.

In order to construct the boiling-point diagram, we still need the functional form of $\lambda_i(T)$. At the boiling point of either pure component $T = T_i$ one has $\mu_i^{v\circ} = \mu_i^{l\circ}$ so that $\lambda_i(T_i) = 0$. By noting that $\big(\partial(\mu/T)/\partial T\big)_p = -h/T^2$ where $h$ is the specific enthalpy, we have

$$\lambda_i(T) = \int_{T_i}^{T}\left(\frac{\partial\lambda_i}{\partial T}\right)_p \mathrm{d}T = \frac{M_i q_i}{R}\int_{T_i}^{T}\frac{\mathrm{d}T}{T^2} = \frac{M_i q_i}{RT_i}\left(1 - \frac{T_i}{T}\right).$$

Here we took into account that the difference of specific enthalpies of the vapor and the liquid phase is equal to the heat of vaporization of a pure component denoted by $q_i$. Since usually $T \approx T_i$, we have $\lambda_i(T) \ll 1$ and $\exp\big(\pm\lambda_i(T)\big) \approx 1 \pm \lambda_i(T) + \lambda_i^2(T)/2$.

For simplicity, we further set $M_Aq_A/RT_A = M_Bq_B/RT_B = \alpha$ and obtain

$$\widetilde{x}_B^{v,l}(T) = \frac{T - T_A}{T_B - T_A} \pm \frac{\alpha(T - T_A)(T - T_B)}{2(T_B - T_A)T} .$$

The first term represents a tieline connecting the boiling points of pure substances and the second one is the deviation of the dew-point curve and the bubble-point curve from the tieline, with + and − giving $\widetilde{x}_B^v$ and $\widetilde{x}_B^l$, respectively.

**Problem 6.11.**
*Calculate the temperature dependence of the mass fraction of the vapor phase in the two-phase region for an ideal binary mixture!*

Mass conservation for each of the components implies that in the two-phase region the mass fraction of the vapor phase $x_v$ is determined by $x_v\widetilde{x}_B^v + (1 - x_v)\,\widetilde{x}_B^l = \widetilde{x}_B$, where $\widetilde{x}_B^v$ and $\widetilde{x}_B^l$ denote the mole fractions of the component $B$ in the gas and in the liquid phase and $\widetilde{x}_B$ is the mole fraction of $B$ outside the two-phase region. We insert the temperature dependence of $\widetilde{x}_B^v(T)$ and $\widetilde{x}_B^l(T)$ calculated in Problem 6.10 to find

$$x_v(T) = \frac{1}{2} - \frac{T\,[T - (1 - \widetilde{x}_B)T_A - \widetilde{x}_B T_B]}{\alpha(T - T_A)(T - T_B)} ,$$

where $T_A$ and $T_B$ are the boiling temperatures of pure components and $\alpha$ denotes the ratios $M_Aq_A/RT_A$ and $M_Bq_B/RT_B$ which are assumed to be the same.

We can also determine the temperature at which, upon heating, bubbles appear in the liquid mixture with composition $\widetilde{x}_B$. In this case $x_v(T) = 0$, giving

$$T_v = \frac{1}{2(\alpha - 2)}\Big\{\alpha\,(T_A + T_B) - 2T_A - 2\widetilde{x}_B\,(T_B - T_A) - \sqrt{[\alpha\,(T_A + T_B) - 2T_A - 2\widetilde{x}_B\,(T_B - T_A)]^2 - 4\alpha(\alpha - 2)T_AT_B}\Big\}.$$

The temperature at which, upon cooling, droplets appear in the vapor mixture with composition $\widetilde{x}_B$ is

$$T_l = \frac{1}{2(\alpha + 2)}\Big\{\alpha\,(T_A + T_B) + 2T_A + 2\widetilde{x}_B\,(T_B - T_A) + \sqrt{[\alpha\,(T_A + T_B) + 2T_A + 2\widetilde{x}_B\,(T_B - T_A)]^2 - 4\alpha(\alpha + 2)T_AT_B}\Big\}.$$

**Problem 6.12.**
*An ideal mixture of fluids A and B, with the mole fraction of the B component equal to* 0.563, *starts to evaporate at* 334 K. *After the first drop of the mixture evaporates, the mole fraction of B in the vapor phase is* 0.484. *Calculate the heats*

*of vaporization for the two components! Pure substances A and B boil at* 329 K *and* 338 K, *respectively, and their kilomolar masses are equal to* 58 kg/kmol *and* 32 kg/kmol, *respectively!*

We use the results of Problem 6.10. We denote the bubble-point temperature in question by $T^*$, the mole fractions of $B$ in the liquid and the vapor phase at this temperature by $\widetilde{x}_B^l$ and $\widetilde{x}_B^v$, respectively, the boiling points of the pure substances by $T_A$ and $T_B$, the kilomolar masses by $M_A$ and $M_B$, and the heats of vaporization by $q_A$ and $q_B$. For $\lambda_i(T) = (M_i q_i/RT_i)(1 - T_i/T) \ll 1$ ($i = A, B$) we have

$$\widetilde{x}_B^v = \lambda_A(T)\frac{1 + \lambda_B(T)/2}{\lambda_A(T) - \lambda_B(T)}$$

and

$$\widetilde{x}_B^l = \lambda_A(T)\frac{1 - \lambda_B(T)/2}{\lambda_A(T) - \lambda_B(T)}\,.$$

From the data we extract $\lambda_A(T^*) = 0.166$ and $\lambda_B(T^*) = -0.151$, which finally give $q_A = 523$ kJ/kg and $q_B = 1107$ kJ/kg. (Substances $A$ and $B$ are acetone and methanol, respectively.)

**Problem 6.13.**

*Metals A and B are perfectly miscible in the melt but they do not mix in the solid phase. Their melting points are at* 660 °C *and* 1400 °C, *respectively. Determine the composition of the melt in coexistence with the crystals of pure metal A (B) at* 610 °C*! What is the lower temperature bound for the existence of the melt? What is the composition of the melt at this temperature? Assume that the melt can be treated as an ideal binary mixture and that* $M_A q_A = M_B q_B = 21.6$ MJ/kmol *in the entire temperature range considered. Here* $M_A$ *and* $M_B$ *denote the kilomolar masses of the metals*; $q_A$ *and* $q_B$ *are the corresponding latent heats of fusion.*

We first consider the coexistence of crystals of metal A and the A-B mixture in the melt. Coexistence implies the equality of the chemical potential of metal A in the solid phase and in the melt:

$$\mu_A^{s\circ} = \mu_A^{l\circ} + \frac{RT}{M_A}\ln \widetilde{x}_A^l\,,$$

where we use the notation analogous to that in Problem 6.10. From here we have

$$\widetilde{x}_A^l = \exp\left(\frac{M_A}{RT}\left(\mu_A^{s\circ} - \mu_A^{l\circ}\right)\right).$$

Like in Problem 6.10 we find that

$$\frac{\mu_A^{s\circ} - \mu_A^{l\circ}}{T} = q_A \left( \frac{1}{T_A} - \frac{1}{T} \right),$$

where $T_A$ is the melting temperature of pure metal A. Consequently,

$$\widetilde{x}_A^l(T) = \exp\left( \frac{M_A q_A}{R} \left( \frac{1}{T_A} - \frac{1}{T} \right) \right).$$

The composition of the melt in coexistence with solid metal B is obtained by swapping indices A and B in the above expression. At 610 °C, the numerical results are $\widetilde{x}_A^l = 0.854$ for the coexistence of solid A and melt and $\widetilde{x}_A^l = 1 - \widetilde{x}_B^l = 0.751$ for the coexistence of solid B and melt.

The thus obtained $\widetilde{x}_A^l(T)$ and $\widetilde{x}_B^l(T)$ determine the locus of the so-called liquidus curves in the temperature-composition phase diagram. For either component, the phase coexistence temperature decreases with decreasing concentration of the component; consequently, the two liquidus curves intersect at a point (referred to as the eutectic point) corresponding to the lowest possible temperature at which a melt can exist. To find the eutectic temperature $T_E$, we equate the $\widetilde{x}_A^l(T)$ obtained from the two liquidus curves

$$\exp\left( \frac{M_A q_A}{R} \left( \frac{1}{T_A} - \frac{1}{T_E} \right) \right) = 1 - \exp\left( \frac{M_B q_B}{R} \left( \frac{1}{T_B} - \frac{1}{T_E} \right) \right),$$

and set $q_A M_A / R = q_B M_B / R \equiv \tau$ to obtain

$$T_E = \frac{\tau}{\ln\left( \exp(\tau/T_A) + \exp(\tau/T_B) \right)} = 581.5\,^\circ\mathrm{C}.$$

The concentration of, e.g., metal A in the eutectic melt is then

$$\widetilde{x}_A^l(T_E) = \exp\left( \tau \left( \frac{1}{T_A} - \frac{1}{T_E} \right) \right) = 0.774.$$

**Problem 6.14.**

*A horizontal cylinder contains* 1 kg *of saturated humid air at* 20 °C. *The cylinder is sealed at the left end and closed by a movable piston on the right; the mass and surface area of the piston are* 10 kg *and* 1 dm$^2$, *respectively. The cylinder is rotated counterclockwise by* 90° *at constant temperature. How much water is condensed in the process? By how much does should the temperature be increased for the water to evaporate again? The ambient pressure is* 1 bar. *The heat of vaporization of water at* 20 °C *is* 2454 kJ/kg *and the saturated vapor pressure at this temperature is*

2337 Pa; *the kilomolar masses of air and water are* 29 kg/kmol *and* 18 kg/kmol, *respectively.*

Each of the components—dry air and water vapor—can be described by the ideal gas equation of state $p_i V = m_i RT/M_i$, where $i = a$ for air and $i = v$ for vapor. In the initial state, the pressure of ambient air $p_0$ is equal to the sum of both partial pressures: $p_0 = p_a + p_v$. At the same time, the partial pressure of vapor $p_v$ is given by the saturated vapor pressure at 20 °C denoted by $p_s$. Thus the initial mass of vapor is

$$m_v = m\left[1 + \left(\frac{p_0}{p_s} - 1\right)\frac{M_a}{M_v}\right]^{-1} = 14.6\ \mathrm{g}\,,$$

where $m = m_a + m_v$ is the initial mass of humid air, whereas $M_v$ and $M_a$ are the kilomolar masses of water and dry air, respectively. After the cylinder is rotated, the pressure inside it increases due to the weight of the piston to $p_0 + \Delta p = p'_a + p_s$ with $\Delta p = m_0 g/A$, where $m_0$ and $A$ denote the mass and the surface area of the piston, respectively. Despite the increase of the total pressure, the partial water vapor pressure remains unaltered and equal to $p_s$ because the temperature is constant. By taking into account that $p'_a V' = (m_a/M_a)RT$ and $p_s V' = (m'_v/M_v)RT$ we obtain the mass of the remaining water vapor:

$$m'_v = m_v\left(\frac{p_0}{p_s} - 1\right)\left(\frac{p_0 + \Delta p}{p_s} - 1\right)^{-1} = 13.3\ \mathrm{g}\,.$$

Thus the mass of water that condenses is $m_v - m'_v \approx 1.3$ g. In order to re-evaporate it, the system must be heated whereby the saturated vapor pressure increases to $p''_s$. Given that $p''_a V'' = (m_a/M_a)RT''$, $p''_a = p_0 + \Delta p - p''_s$, and $p''_s V'' = (m_v/M_v)RT''$, we have

$$p''_s = p_s\left(1 + \frac{\Delta p}{p_0}\right) \approx 2570\ \mathrm{Pa}\,.$$

The temperature increase needed is calculated from the Clausius–Clapeyron equation:

$$T'' - T \approx \left(\frac{p''_s}{p_s} - 1\right)\frac{RT^2}{q_v M_v} = 1.6\,^\circ\mathrm{C}\,,$$

where $q_v = 2454$ kJ/kg denotes the heat of vaporization of water at 20 °C.

**Problem 6.15.**
*Calculate the decrease of the melting point of ice after air is replaced by pure nitrogen at* 200 bar*! At air pressure of* 1 bar *and* 0 °C, 23 ml *of nitrogen dissolve in one liter of water. The heat of fusion of ice is* 336 kJ/kg; *the densities of ice and water are* 917 kg/m$^3$ *and* 1000 kg/m$^3$, *respectively. Nitrogen does not dissolve in ice.*

The melting point of ice is shifted to a lower temperature because it directly depends on pressure as dictated by the Clausius–Clapeyron equation and because more nitrogen is dissolved in water at a higher pressure, which additionally decreases the chemical potential of water as a solvent. We have

$$\Delta T = \frac{\mathrm{d}T}{\mathrm{d}p}\,\Delta p - \frac{RT^2}{M_1 q_f} x_1 ,$$

where $M_1$ is the kilomolar mass of nitrogen and $x_1$ is its mass fraction. From the Clausius–Clapeyron equation $\mathrm{d}p/\mathrm{d}T = q_f/\left[T(1/\rho_l - 1/\rho_s)\right]$ and Henry's law $x_1/x_1' = p_1/p_1'$, where $x_1'$ denotes the reference concentration of nitrogen in water at a reference pressure $p_1'$ and $p_1$ is the pressure of the pure-nitrogen atmosphere, we obtain

$$\Delta T = -\frac{T}{q_f}\left[\left(\rho_s^{-1} - \rho_l^{-1}\right)(p_1 - p_0) + \frac{V_1}{m_2}\frac{p_0}{p_1'} p_1\right] .$$

Here $p_0$ stands for the initial air pressure, $p_1' = 0.829$ bar is the partial nitrogen pressure in the air atmosphere, and $V_1$ is the volume of nitrogen dissolved at $p_0$ in a body of water of mass $m_2$.

With the given data the first term is approximately three times larger than the second one; we find that $\Delta T = -1.91$ K.

## Problem 6.16.

*The electrochemical process in a galvanic cell is summarized by a redox reaction* $\mathrm{Zn}^{(s)} + \mathrm{Cu}^{2+(aq)} \rightleftharpoons \mathrm{Zn}^{2+(aq)} + \mathrm{Cu}^{(s)}$. *At* 25 °C *and* 1 bar *the Gibbs free energy of reaction* $\Delta G_r$ *and the enthalpy of reaction* $\Delta H_r$ *are equal to* $-212.55$ kJ/mol *and* $-218.66$ kJ/mol, *respectively. If the mole fractions of the* $\mathrm{Zn}^{2+}$ *and the* $\mathrm{Cu}^{2+}$ *ions in solution are equal to* $10^{-2}$ *and to* $10^{-4}$, *respectively, the reaction is not in equilibrium and there is a nonzero electric current between the zinc and copper electrodes connected by a wire. What external electric voltage must be applied between the electrodes to stop the redox reaction and consequently the electric current? By how much does this voltage change if the temperature of the galvanic cell is increased by* 1 K *at constant pressure if the mole fractions of both types of ions are unchanged? Assume that the solutions are ideal!*

Suppose that d$n$ moles of solid zinc react with copper ions in solution to give d$n$ moles of zinc ions in solution and the corresponding amount of solid copper. The change of the Gibbs free energy in such a process reads

$$\mathrm{d}G = \mathrm{d}n\left(-\mu_{\mathrm{Zn}} M_{\mathrm{Zn}} - \mu_{\mathrm{Cu}^{2+}} M_{\mathrm{Cu}} + \mu_{\mathrm{Zn}^{2+}} M_{\mathrm{Zn}} + \mu_{\mathrm{Cu}} M_{\mathrm{Cu}}\right) .$$

In an ideal solution, the chemical potential of zinc ions is given by $\mu_{\mathrm{Zn}^{2+}} = \mu^{\circ}_{\mathrm{Zn}^{2+}} + (RT/M_{\mathrm{Zn}^{2+}}) \ln \widetilde{x}_{\mathrm{Zn}^{2+}}$, where $\mu^{\circ}_{\mathrm{Zn}^{2+}}$ is the chemical potential in a pure substance and

$\widetilde{x}_{\mathrm{Zn}^{2+}}$ is the mole fraction of zinc ions in solution. (An analogous relation holds for the copper ions $\mathrm{Cu}^{2+}$.) Then

$$\mathrm{d}G = \mathrm{d}n \left[ \Delta G_r(T, p) + RT \ln \frac{\widetilde{x}_{\mathrm{Zn}^{2+}}}{\widetilde{x}_{\mathrm{Cu}^{2+}}} \right],$$

where $\Delta G_r(T, p)$ denotes the Gibbs free energy of reaction at a given temperature and pressure. Under the given conditions and for $\mathrm{d}n > 0$ one obtains $\mathrm{d}G < 0$; therefore, the redox reaction indeed proceeds from left to right and the electrical charge transferred in the process is equal to $\mathrm{d}e = 2N_A e_0 \mathrm{d}n$ (recall that $e_0 = 1.6 \times 10^{-19}$ As). In other words, $\mathrm{d}G$ corresponds to the amount of electrical work that the galvanic cell can expend $\phi \mathrm{d}e$, where $\phi$ is the voltage between the electrodes. Alternatively, an external battery of the same voltage but opposing polarity may be connected to the electrodes to stop the redox reaction and consequently the electric current, like in a compensation measurement of voltage. Finally, we arrive at the so-called Nernst equation giving the cell voltage

$$\phi(T, p) = \frac{1}{2N_A e_0} \left[ \Delta G_r(T, p) + RT \ln \frac{\widetilde{x}_{\mathrm{Zn}^{2+}}}{\widetilde{x}_{\mathrm{Cu}^{2+}}} \right] = -1.048 \text{ V}.$$

If the two mole fractions are equal, $\widetilde{x}_{\mathrm{Zn}^{2+}} = \widetilde{x}_{\mathrm{Cu}^{2+}}$, the setup is known as the Daniell cell with a voltage of $-1.107$ V at standard conditions (25 °C and 1 bar). In our case, however, $\widetilde{x}_{\mathrm{Zn}^{2+}} \neq \widetilde{x}_{\mathrm{Cu}^{2+}}$, which leads to a small correction of voltage of $+0.059$ V. (If the electrodes were made from the same metal, one would have $\Delta G_r = 0$. However, a nonzero voltage still appears between the electrodes if the two mole fractions are different, which is exploited in the so-called concentration cell.)

Note that the cell voltage is temperature-dependent. Apart from the explicit temperature dependence in the logarithmic term of the Nernst equation, the Gibbs free energy of reaction too changes with temperature. At constant pressure, the corresponding change is obtained from

$$\Delta G_r(T) - \Delta G_r(T') = \int_T^{T'} \left( \frac{\partial \Delta G_r}{\partial T} \right)_p \mathrm{d}T = -\int_T^{T'} \Delta S_r(T)_p \mathrm{d}T.$$

Here the entropy of reaction $\Delta S_r = (\Delta H_r - \Delta G_r)/T$ is calculated from the data given at 25 °C (note that $\Delta T = T - T' = 1$ K is rather small) to give the new value of $\Delta G_r$ and finally the total change of the voltage of galvanic cell, which is $+0.3$ mV. (The magnitude of voltage decreases with temperature.)

# Chapter 7
# Transport Phenomena

**Problem 7.1.**

*The temperature gradient at the surface of the Earth is equal to* 0.03 K/m. *Calculate the temperature in the center of Earth, assuming that it is homogeneous and that the distribution of the heat-emitting radioactive substances is uniform! The thermal conductivity coefficient is* 1 W/mK.

The stationary temperature profile is described by $-\lambda\nabla^2 T = q$, where $\lambda$ is the thermal conductivity coefficient and $q$ is the internal heat source, i.e., heat generated per unit time per unit volume. Due to spherical symmetry, we have $\mathrm{d}^2T/\mathrm{d}r^2 + (2/r)\,\mathrm{d}T/\mathrm{d}r = -q/\lambda$ which gives $T(r) = -(q/6\lambda)r^2 + const.$ The constant of integration is determined by the condition that in equilibrium, the heat radiated into space must be equal to the total heat generated by the radioactive sources which leads to $4\pi R^3 q/3 = 4\pi R^2\sigma\,[T(R)]^4$. This gives

$$T(r) = -\frac{1}{2R}\left.\frac{\mathrm{d}T}{\mathrm{d}r}\right|_{r=R}\left(R^2 - r^2\right) + \left(-\frac{\lambda}{\sigma}\left.\frac{\mathrm{d}T}{\mathrm{d}r}\right|_{r=R}\right)^{1/4},$$

where $R \approx 6400$ km is the diameter of the Earth and $\mathrm{d}T/\mathrm{d}r|_{r=R} < 0$ is the gradient of temperature at the surface. We find that the temperature in the center of the Earth exceeds the surface temperature by $9.6\times10^4$ K. Note that in this model, the surface temperature is severely underestimated: $T(R) = [(\lambda/\sigma)\mathrm{d}T/\mathrm{d}r|_{r=R}]^{1/4} = 27$ K.

**Problem 7.2.**

*Light shines onto one side of a one-meter-thick layer of ice surrounded by air at* $-10\,^\circ$C. *Calculate the highest temperature within the layer if the incident energy flux is equal to* 100 W/m$^2$*! The absorption coefficient for light in ice is* 2 m$^{-1}$; *the thermal conductivity coefficient of ice is* 2.2 W/mK.

The stationary temperature profile is given by the diffusion equation $\mathrm{d}^2T/\mathrm{d}z^2 = -q(z)/\lambda$, where $z$ denotes the distance from the irradiated surface, $q(z)$ is the

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internal heat source, and $\lambda$ is the thermal conductivity coefficient. The absorbed light can be represented by an internal heat source $q = -\mathrm{d}j/\mathrm{d}z = \mu j$, yielding $j = j_0 \exp(-\mu z)$ and $q = \mu j_0 \exp(-\mu z)$. The solution of the heat equation reads $T(z) = -j_0 \exp(-\mu z)/\lambda\mu + az + b$, with boundary conditions $T(0) = T(h) = T_0$ where $T_0$ denotes the ambient air temperature. Finally,

$$T(z) = \frac{j_0}{\lambda\mu}\left\{1 - \exp(-\mu z) - \frac{z}{h}\left[1 - \exp(-\mu h)\right]\right\} + T_0\,.$$

The highest temperature within the layer is at a distance

$$z_{\max} = -\frac{1}{\mu}\ln\Big(\left[1 - \exp(-\mu h)\right]/\mu h\Big) = 0.419\ \mathrm{m}$$

from the irradiated surface and is equal to $-5.36\,^\circ\mathrm{C}$.

**Problem 7.3.**

*Water flows through a* 10 m*-long tube with inner diameter* 2 cm *and wall thickness* 1 cm. *The temperature of water at inlet is* $100\,^\circ\mathrm{C}$ *and the outside temperature is* $0\,^\circ\mathrm{C}$. *Calculate the temperature of water at outlet if the flow rate through the tube is* 2 l/s*! The thermal conductivity coefficient of the wall is* 6 W/mK.

We assume that the decrease in water temperature is small, which will be justified *a posteriori*. Furthermore, the water temperature across the transverse cross section of the tube is approximately constant since the flow is turbulent. To support this statement we note that between the melting and boiling point of water its viscosity is equal to $\sim 10^{-3}$ Ns/kgm. Then the Reynolds number is $\mathrm{Re} = 2\rho v r_1/\eta = 1.27 \times 10^5 \gg 1$, where $r_1$ is the inner radius of the tube. The large value of Re implies turbulent flow, and thus one can safely assume that the water temperature at the inner side of the wall is $100\,^\circ\mathrm{C}$.

The rate of heat flow though a closed cylindrical surface at any point within the wall must not depend on its radius:

$$\dot{Q} = \int \mathbf{j}\cdot \mathrm{d}\mathbf{A} = -\lambda\frac{\mathrm{d}T}{\mathrm{d}r}A = -2\pi\lambda h r\frac{\mathrm{d}T}{\mathrm{d}r}$$

so that $\mathrm{d}T/\mathrm{d}r = -\dot{Q}/2\pi\lambda h r$; here $h$ denotes the tube length. By taking into account the boundary conditions $T(r_1) = T_1$ and $T(r_2) = T_2$, where $r_1$ and $r_2$ are the inner and the outer radii of the tube, respectively, whereas $T_1$ and $T_2$ are the water temperature and the ambient temperature, respectively, we obtain

$$T(r) = \frac{T_2 - T_1}{\ln(r_2/r_1)}\ln(r/r_1) + T_1$$

and $\dot{Q} = -2\pi\lambda h(T_2 - T_1)/\ln(r_2/r_1)$. Due to the flow of heat into the environment, water is cooled: $\dot{Q} = -(\mathrm{d}m/\mathrm{d}t)c_p\,\Delta T = -\rho\Phi_V c_p\,\Delta T$. We find that

$$\Delta T = \frac{2\pi\lambda h(T_2 - T_1)}{\rho \Phi_V c_p \ln(r_2/r_1)} = -6.47\,\mathrm{K}\,.$$

This result is approximate since it was obtained by neglecting the decrease of water temperature along the tube. However, as $\Delta T$ is small the error is not very large. A more accurate calculation that takes into account the temperature variation along the tube yields $\Delta T = -6.27$ K.

### Problem 7.4.

*How much time does it take for a* 10 cm*-thick ice layer to grow on a lake surface? The water temperature is* 0 °C *and the temperature of the wind blowing across the lake is* −2 °C. *The thermal conductivity coefficient of ice is* 1.6 W/mK, *its density is* 917 $\mathrm{kg/m^3}$, *and the heat of fusion is* 336 kJ/kg.

The wind ensures that the temperature of air is constant. Due to the upward heat flow through the ice, water freezes at the bottom of the layer of ice. The heat flux is given by $j = -\lambda\,\mathrm{d}T/\mathrm{d}z$, where $z$ is the distance from the water–ice interface. Since $j$ cannot depend on $z$, $T \propto z$ and

$$|j| = \lambda \frac{\Delta T}{h}\,,$$

where $\Delta T$ is the difference between the temperatures of water and wind whereas $h$ is the thickness of ice. The heat removed from water by conduction equals the heat released by freezing: $q_f\,\mathrm{d}m = A|j|\,\mathrm{d}t$ or $h\,\mathrm{d}h = (\lambda\,\Delta T/q_f\rho_s)\,\mathrm{d}t$, where $\rho_s$ is the density of ice, $q_f$ is the heat of fusion, and $A$ is the surface area. By integrating from the initial state with no ice to the final state where the thickness of the ice layer is $h$ we obtain

$$t = \frac{q_f \rho_s h^2}{2\lambda\,\Delta T} = 4.8 \times 10^5\ \mathrm{s}\,.$$

### Problem 7.5.

*A large* 10 cm*-thick copper plate with electrical resistivity* $\zeta = 1.68 \times 10^{-8}\ \Omega\mathrm{m}$ *and thermal conductivity coefficient* 400 W/mK *carries an electric current of density* $j_e$*. One side of the plate is thermally insulated, whereas the other one is covered by a* 2 mm*-thick layer of ice which, in turn, is in contact with air at* −10 °C *and* 1 bar. *Calculate the threshold value of* $j_e$ *for the ice to melt! What is the highest temperature within the copper plate at the threshold* $j_e$*? The thermal conductivity coefficient of ice is* 2.2 W/mK, *the density of ice is* 920 $\mathrm{kg/m^3}$, *and the heat of fusion* 336 kJ/kg. *Recall that in Joule heating, the power per unit volume is equal to* $\zeta j_e^2$*.*
*—How does the threshold change when the air pressure is increased to* 100 bar*?*

We denote the thicknesses of plate and ice layer by $d$ and $d'$, respectively; the $z$ axis points along the normal of the plate and the ice layer, with the origin at the contact of the plate and the insulation. The local temperature at this contact is $T_0$, the temperature at the copper–ice contact is $T_1$, and the ambient air temperature is $T_2$. Due to the single-sided thermal insulation, all Joule heat generated within the plate is released into the ambient air through the ice layer; one can expect that $T_0 > T_1 > T_2$.

There are no heat sources in the ice layer; therefore the temperature profile within this layer must be a linear function of $z$. On the other hand, the internal heat source due to Joule heating in the copper plate is given by $q = \zeta j_e^2$. The temperature profile within the plate is described by the diffusion equation $\mathrm{d}^2T/\mathrm{d}z^2 = -q/\lambda$, where $\lambda$ is the thermal conductivity coefficient of copper. By integrating twice we have $T(z) = -qz^2/2\lambda + az + b$, where $a$ and $b$ are constants to be determined from boundary conditions: Perfect insulation at $z = 0$ imposes $(\mathrm{d}T/\mathrm{d}z)(0) = 0$, whereas the continuity of the heat flux at the copper–ice contact means that $\lambda(\mathrm{d}T/\mathrm{d}z)(d) = \lambda'(T_2 - T_1)/d'$, where $\lambda'$ is the thermal conductivity coefficient of ice. Finally, the temperature profile in copper reads

$$T(z) = T_2 + \frac{q(d^2 - z^2)}{2\lambda} + \frac{qdd'}{\lambda'} .$$

Within the ice layer, temperature is highest at the copper–ice contact and to ensure that the ice does not melt, this temperature denoted by $T_1$ must not exceed the melting point at 1 bar, which is 0 °C. This leads to the requirement that $q < \lambda'(T_m - T_2)/dd' = 110\ \mathrm{kW/m^3}$ or $j_e < 2.56 \times 10^6\ \mathrm{A/m^2}$. Under these conditions, the highest temperature in the copper plate is measured just next to the insulation and is $T_0 = 1.4\,°\mathrm{C}$. —According to the Clausius–Clapeyron equation, an increase of the air pressure to 100 bar decreases the melting point by about 0.7 K. The corresponding threshold current density is $j_e' = 2.47 \times 10^6\ \mathrm{A/m^2}$.

### Problem 7.6.

*How much time does it take for a* 0.2 mm*-diameter water droplet to evaporate at* 20 °C, *provided that the ambient air is dry and that there is no wind so that the only mode of motion of water molecules in air is diffusion? Assume that the distribution of vapor around the droplet is stationary at all times, and neglect any effects of gravity. The diffusion coefficient is* $0.2 \times 10^{-4}\ \mathrm{m^2/s}$, *the saturated vapor pressure at* 20 °C *is* 24 mbar, *and the surface tension of water is* 0.073 N/m. *How long does the droplet evaporate in saturated humid rather than dry air?*

The vapor pressure next to the droplet exceeds the saturated vapor pressure $p_s$ by $\Delta p$. The equilibrium between liquid water and vapor requires that their chemical potentials are the same so that $\Delta p/\rho_v = \Delta p_l/\rho_l = 2\gamma/r_0\rho_l$ (Problem 4.15) or $\Delta p = 2\gamma\rho_v/r_0\rho_l$, where $\rho_v = p(r_0)M/RT$ and $\rho_l$ denote the densities of vapor and liquid water, respectively; $\gamma$ stands for the surface tension and $r_0$ is the droplet radius. This gives

$$p(r_0) = p_s\left(1 - \frac{2\gamma}{r_0}\frac{M}{RT\rho_l}\right)^{-1} .$$

The pressure gradient drives the mass flux $\mathbf{j} = -D\nabla\rho_v$, which is spherically symmetric with $j_r = -(DM/RT)\,\mathrm{d}p/\mathrm{d}r$, where we replaced $\rho_v$ by $pM/RT$. The total mass flow rate from the droplet must not depend on $r$:

$$\Phi_m = \int \mathbf{j}\cdot \mathrm{d}\mathbf{A} = -4\pi r^2 \frac{DM}{RT}\frac{\mathrm{d}p}{\mathrm{d}r} = const.$$

or $(\Phi_m/r^2)\,\mathrm{d}r = -(4\pi DM/RT)\,\mathrm{d}p$. We integrate the left-hand side from $r_0$ to $\infty$ and the right-hand side from $p(r_0)$ to $p_\infty$, where $p_\infty$ stands for the vapor pressure far from the droplet. This gives

$$\Phi_m = 4\pi r_0 \frac{DM}{RT}\left[p(r_0) - p_\infty\right].$$

In a perfectly dry ambient air, $p_\infty = 0$. We take into account that $\Phi_m = -\mathrm{d}m/\mathrm{d}t = -4\pi r_0^2 \rho_l\,\mathrm{d}r_0/\mathrm{d}t$, rearrange the obtained equality, and integrate it from 0 to $t$ and from the initial droplet radius $a$ to 0 where the droplet vanishes. Finally

$$\begin{aligned} t &= -\frac{RT\rho_l}{DM}\int_a^0 \frac{r_0\,\mathrm{d}r_0}{p(r_0)} = -\frac{RT\rho_l}{DMp_s}\int_a^0 \left(1 - \frac{2\gamma}{r_0}\frac{M}{RT\rho_l}\right) r_0\,\mathrm{d}r_0 \\ &= \frac{RT\rho_l a^2}{2DMp_s}\left(1 - \frac{4\gamma M}{aRT\rho_l}\right) = 14\ \mathrm{s}. \end{aligned}$$

In saturated humid air, $p_\infty = p_s$ and the dependence of the mass flow rate on $r_0$ is different from that in dry air. In this case we find that

$$\begin{aligned} t &= -\frac{RT\rho_l}{DMp_s}\int_a^0 \left(\frac{r_0}{2\gamma}\frac{RT\rho_l}{M} - 1\right) r_0\,\mathrm{d}r_0 \\ &= \frac{RT\rho_l a^2}{2DMp_s}\left(\frac{aRT\rho_l}{3\gamma M} - 1\right) = 8.7 \times 10^5\ \mathrm{s}. \end{aligned}$$

**Problem 7.7.**

*Consider two parallel layers of ice separated by a* 1 cm-*thick layer of still air at a pressure of* 1 bar. *The temperature of the top layer is* 0 °C, *whereas the bottom layer is cooled and at a constant temperature of* −15 °C. *The saturated vapor pressures at these two temperatures are* 6 mbar *and* 4 mbar, *respectively. Estimate the thickness of ice transferred from the top to the bottom layer in one hour! The diffusion coefficient for water in air is equal to* $0.2\ \mathrm{cm^2/s}$ *and the density of ice is* $916\ \mathrm{kg/m^3}$.

We denote the thickness of the air layer by $h$ and the distance from the bottom layer of ice by $z$. The temperature gradient results in a difference of saturated vapor pressures across the air layer and thus to a variation of vapor density $\rho(z)$ across the air. Under stationary conditions, the diffusion equation reads $\mathrm{d}^2\rho/\mathrm{d}z^2 = 0$ with boundary conditions $\rho_1 = \rho(0)$ and $\rho_2 = \rho(h)$; this gives $\rho(z) = \rho_1 + (\rho_2 - \rho_1)z/h$. As a consequence, a mass flux of vapor $j = D(\rho_2 - \rho_1)/h$ is established between the two layers of ice (here $D$ stands for the diffusion constant of water in air), which results in the thinning of the top layer of ice and the concomitant thickening of the bottom layer. The mass of ice per unit area transferred in time $t$ is equal to $\rho_s\delta = jt = Dt(\rho_2 - \rho_1)/h$, where $\delta$ denotes the change of thicknesses of the layers of ice and $\rho_s$ is the density of ice. We use the ideal-gas equation of state $\rho_i = p_i M/RT_i$ $(i = 1, 2)$ to relate the vapor density next to the walls $\rho_i$ with the corresponding vapor pressures $p_i$. Here we assume that the temperature of vapor at each wall is equal to the temperature of the ice layer $T_i$; $M = 18$ kg/kmol is the kilomolar mass of water. Finally, we obtain

$$\delta = \frac{Dt}{\rho_s h}(\rho_2 - \rho_1) = \frac{DMt}{\rho_s hR}\left(\frac{p_2}{T_2} - \frac{p_1}{T_1}\right) \approx 11\,\mu\text{m}\,.$$

**Problem 7.8.**
*Discuss the transport phenomena in a thermocouple: The Seebeck, the Peltier, and the Thomson effect! —The temperature dependence of the copper–constantan thermocouple voltage is given by* $\phi_T(T) = a(T - T_0) + b(T - T_0)^2$ *with* $a = 37.54$ $\mu$V/K, $b = 0.0445$ $\mu$V/K$^2$, *and* $T_0 = 0\,°$C. *Calculate the Peltier coefficient as well as the difference of the Thomson coefficients at* 20 °C*!*

Consider an electric circuit formed by two different wires $A$ and $B$ (Fig. 7.1). If the temperatures of the two $A - B$ junctions $T_1$ and $T_2$ are not equal, a voltage $\phi_T$ appears in the circuit (the Seebeck effect). This voltage is proportional to the difference of the temperatures of the junctions and the corresponding proportionality factor $S_{AB}$ is referred to as the Seebeck coefficient: $\phi_T = S_{AB}(T_2 - T_1)$. On the other hand, the junction temperatures may be maintained equal while driving an electric current $I$ through the circuit. In this case one of the junctions releases heat at a flow rate $P$ while the other junction absorbs heat at the same rate (the Peltier effect). The flow rate $P$ is proportional to the electric current $I$, the proportionality factor being the Peltier coefficient $\Pi_{AB}$. The Peltier effect originates in the contact potential (i.e., the difference of the Fermi level of electrons) at the $A - B$ junction which corresponds to the Peltier coefficient $\Pi_{AB}$, whereas the Seebeck effect stems from the temperature variation of the contact potential and the thermodiffusion or the Thomson effect. In thermodiffusion, a temperature gradient along each wire results in a difference of electron density, giving rise to an additional voltage $\int_{T_1}^{T_2}\sigma_i(T)\,\mathrm{d}T$ $(i = \mathrm{A, B})$. By writing the Kirchhoff law for a closed circuit, we obtain $\phi_T = S_{AB}(T_2 - T_1) = \Pi_{AB}(T_2) - \Pi_{AB}(T_1) + \int_{T_1}^{T_2}(\sigma_A - \sigma_B)\,\mathrm{d}T$ or

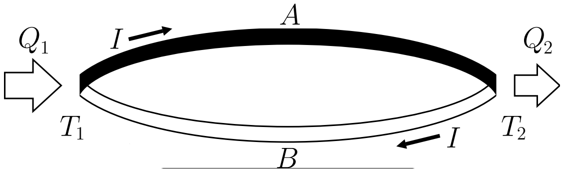

Fig. 7.1 Schematic of the transport phenomena in a thermocouple: The hot junction exchanges more heat with the environment than the cold contact

$$\frac{\mathrm{d}\phi_T}{\mathrm{d}T} = S_{AB} = \frac{\mathrm{d}\Pi_{AB}(T)}{\mathrm{d}T} + \sigma_A(T) - \sigma_B(T)\,.$$

If the temperatures of the two junctions differ, more heat is exchanged with the environment at the hot junction than at the cold one. In this case a thermocouple acts as a reversible heat engine if Ohmic loss is neglected. Now we consider the junctions at temperatures $T$ and $T + \Delta T$ where $\Delta T \ll T$ and we examine the entropy balance for electrons in the circuit that carries an electric current $I$:

$$\Delta S = -\frac{\sigma_A(T) I \, \Delta T}{T} + \frac{\sigma_B(T) I \, \Delta T}{T} + \frac{\Pi_{AB}(T) I}{T} - \frac{\Pi_{AB}(T + \Delta T) I}{T + \Delta T} = 0 \, .$$

The first two terms originate in thermodiffusion and the last two in contact potential; since we consider a cyclic process for electrons it follows that $\Delta S = 0$. For an infinitesimally small temperature difference we have

$$\sigma_B(T) - \sigma_A(T) = T \frac{\mathrm{d}}{\mathrm{d}T} \left( \frac{\Pi_{AB}}{T} \right)$$

and

$$\frac{\mathrm{d}\phi_T}{\mathrm{d}T} = S_{AB} = \frac{\Pi_{AB}(T)}{T}$$

as well as

$$\frac{\mathrm{d}^2\phi_T}{\mathrm{d}T^2} = \frac{\sigma_B(T) - \sigma_A(T)}{T} \, .$$

The first and the second derivative of $\phi_T$ can be measured experimentally so as to determine the temperature dependencies of $\Pi_{AB}$ and $\sigma_B - \sigma_A$. With the functional form of $\phi_T(T)$ given at the beginning, we obtain $\Pi_{AB}(T) = [a + 2b\,(T - T_0)]\,T = 11.5$ mV and $\sigma_B(T) - \sigma_A(T) = 2bT = 26.1\ \mu\text{V/K}$ at $T = 20\,^\circ\text{C}$.

The derivative $\mathrm{d}\phi_T/\mathrm{d}T$ can also be derived in a different way. One can use the Onsager reciprocal relations to analyze the simultaneous transport of electric charge and heat. The heat flow rate and the electric current (denoted by $P$ and $I$, respectively) are both driven by a temperature difference $\Delta T$ and a voltage $\phi$; temperature is equal to $T$. We have

$$P = -L_{11}\frac{\Delta T}{T^2} - L_{12}\frac{\phi}{T}$$

and

$$I = -L_{21}\frac{\Delta T}{T^2} - L_{22}\frac{\phi}{T} \, ,$$

where $L_{ij}$ are the transport coefficients and $L_{ij} = L_{ji}$. The thermovoltage can be measured by a compensation measurement where the electric current vanishes ($I = 0$); this gives $\phi = -\phi_T = -S_{AB}\,\Delta T$ and thus $S_{AB} = (L_{21}/L_{22})/T$. On the other hand, the Peltier effect is observed at $\Delta T = 0$ where $P = -L_{12}\phi/T$ and $I = -L_{22}\phi/T$. The final result

$$\Pi_{AB} = \frac{P}{I} = \frac{L_{12}}{L_{22}} = \frac{L_{21}}{L_{22}} = T S_{AB}$$

is a special case of Onsager reciprocal relations $L_{ij} = L_{ji}$ which are based on the time-reversal invariance of the fundamental laws of physics. At the same time, we recall that in the derivation that involves the entropy balance, one needs to assume that charge transfer is reversible instead of relying on the relation $L_{ij} = L_{ji}$.

### Problem 7.9.

*A* 20 cm-*diameter black sphere suspended in vacuum is surrounded by a thin black concentric shell* 30 cm *in diameter. What is the rate of radiative cooling compared to that of a bare sphere? The space between the sphere and the shell is evacuated.*

We denote the temperatures of the sphere and the shell by $T_1$ and $T_2$, respectively. The net rate of heat flow from the sphere to the shell is equal to the difference between the emitted and the absorbed power: $P_1 = A_1\sigma\left(T_2^4 - T_1^4\right)$, where $A_1 = 4\pi r_1^2$ is the surface area of the sphere of radius $r_1$ and $\sigma$ is the Stefan–Boltzmann constant. The rate of heat flow emitted by the shell toward outside is $P_2 = -A_2\sigma T_2^4$; $A_2 = 4\pi r_2^2$ is the surface area of the shell. In the stationary state, one has $P_1 = P_2$ if the shell temperature is to remain constant. This leads to $A_1T_2^4 - A_1T_1^4 = -A_2T_2^4$ and $T_2^4 = A_1T_1^4/\left(A_1 + A_2\right)$. The ratio of the rate of heat flow from the shell towards outside and that of a bare sphere is

$$\frac{P_2}{P_1} = \frac{A_2T_2^4}{A_1T_1^4} = \frac{A_2}{A_1 + A_2} = \frac{r_2^2}{r_1^2 + r_2^2} = 0.692\,.$$

If the shell radius is only infinitesimally larger than the radius of the sphere, we have $P_2/P_1 = 1/2$ which agrees with the limit of planar surfaces.

### Problem 7.10.

*The insulation of a Dewar flask can be greatly improved by placing a thin silvered metal shield into the evacuated gap between the silvered flask walls. How many shields are needed if the losses due to heat flow are to be reduced by* 90%*?*

This problem can be solved by mathematical induction. We first consider a shield at a temperature $T_2$ placed between the walls of temperatures of $T_1$ and $T_3 > T_1$. The rate of heat flow from the hot wall to the shield is equal to $P_{32} = A\sigma a\left(T_3^4 - T_2^4\right)$, whereas the rate of heat flow from the shield to the cold wall is $P_{21} = A\sigma a\left(T_2^4 - T_1^4\right)$; here $A$ denotes the surface area of the walls and $a$ is the absorption coefficient. In the stationary state one has $P_{32} = P_{21}$ or $T_3^4 - T_2^4 = T_2^4 - T_1^4$, hence $T_2^4 = \left(T_1^4 + T_3^4\right)/2$. The rate of heat flow is then given by $P_{21} = A\sigma a\left(T_3^4 - T_1^4\right)/2$, i.e., half of the value in the shield-free configuration.

In the two-shield configuration, the rate of heat flow from the hot wall at a temperature $T_4$ to the first shield at a temperature $T_3$ is $P_{43} = A\sigma a\left(T_4^4 - T_3^4\right)$, whereas the rate of heat flow from the first shield to the second one at a temperature $T_2$ is $P_{32} = A\sigma a\left(T_3^4 - T_2^4\right)$ and the rate of heat flow from the second shield to the cold wall at a temperature $T_1$ is $P_{21} = A\sigma a\left(T_2^4 - T_1^4\right)$. In the stationary state all three rates have to be equal, which gives $T_2^4 = 2T_1^4/3 + T_4^4/3$ and $P_{21} = A\sigma a\left(T_4^4 - T_1^4\right)/3$. In other words, the rate of heat flow is now a third of that in the shield-free configuration.

We conclude that the rate of heat flow between walls with $n$ shields is $1/\,(n+1)$-th part the rate in the shield-free configuration:

$$P = \frac{P_0}{n+1}\,.$$

In order to reduce heat losses by 90%, one needs to install 9 shields between the walls of the flask.

# Part II
# Statistical Physics

# Chapter 8
# Classical Canonical Ensemble

**Problem 8.1.**
*An infinite vertical cylinder is filled with an ideal monatomic gas. Calculate the heat capacity of the gas, assuming that its temperature and the gravitational acceleration do not depend on height! Also consider a cylinder of finite height as well as the case in which the gravitational acceleration varies with height!*

The phase space of a $N$-particle monatomic gas is spanned by $6N$ coordinates: 3 coordinates specify the position of each atom ($\mathbf{r}_i$) and 3 coordinates give the corresponding linear momentum ($\mathbf{p}_i$); $i = 1, \dots N$. As the gas is in thermal equilibrium with the environment, it has a well-defined (and constant) temperature. Therefore its behavior is governed by the canonical probability density $\rho(E) \propto \exp(-\beta E)$ which depends only on energy $E$ and temperature; $\beta = 1/k_B T$. The energy contains the kinetic and the potential terms: $E = \sum_{i=1}^N \left(\mathbf{p}_i^2/2m + mgz_i\right)$; here the $z$-axis points in the direction opposite to that of the gravitational acceleration $\mathbf{g}$, and $m$ denotes the mass of a single atom. To calculate the internal energy and the heat capacity, one must first evaluate the partition function $\exp\left(-\beta F\right) \propto \int \exp(-\beta E)\,\mathrm{d}\Gamma$, where $\mathrm{d}\Gamma = \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{p}_1 \cdots \mathrm{d}\mathbf{r}_N \mathrm{d}\mathbf{p}_N$ is the element of the phase space. Since the atoms are independent and identical, the index $i$ can be dropped and we have

$$\exp\left(-\beta F\right) \propto \left[\iint_A \mathrm{d}x\,\mathrm{d}y \int_0^\infty \mathrm{d}z \int_{-\infty}^\infty \mathrm{d}p_x \int_{-\infty}^\infty \mathrm{d}p_y \int_{-\infty}^\infty \mathrm{d}p_z \right.$$

$$\left. \times \exp\left(-\beta\left(\frac{p_x^2 + p_y^2 + p_z^2}{2m} + mgz\right)\right)\right]^N$$

$$= \left\{ A \int_0^\infty \exp\left(-\beta mgz\right) \mathrm{d}z \left[\int_{-\infty}^\infty \exp\left(\frac{\beta p_x^2}{2m}\right) \mathrm{d}p_x\right]^3 \right\}^N$$

G. Skačej and P. Ziherl, *Solved Problems in Thermodynamics and Statistical Physics*, https://doi.org/10.1007/978-3-030-27661-4_8

because the integrals over the different components of the linear momentum are all independent. In the above result, $A$ is the horizontal cross section of the cylinder. Given that $\int_{-\infty}^{\infty} \exp(-a^2x^2)\,\mathrm{d}x = \sqrt{\pi}/a$, we find that

$$\exp(-\beta F) \propto A^N \left[\frac{(2\pi)^{3/2} m^{1/2}}{g\beta^{5/2}}\right]^N .$$

After taking the logarithm of this result, we calculate the average energy $\langle E\rangle = (\partial \beta F/\partial\beta)_V = 5N/2\beta = 5Nk_BT/2$; this represents the internal energy $U$. Thus the heat capacity is

$$c_V = \frac{1}{Nm}\left(\frac{\partial U}{\partial T}\right)_V = \frac{5k_B}{2m} = \frac{5N_Ak_B}{2M} = \frac{5R}{2M} .$$

Here $M$ denotes the kilomolar mass of the gas, $N_A = 6 \times 10^{26}$ kmol$^{-1}$ is the Avogadro number, and $R$ is the gas constant. (If the potential energy is excluded, the above results would read $\langle E\rangle = 3Nk_BT/2$ and $c_V = 3R/2M$, which agrees with the equipartition theorem.)

In a cylinder of height $L$ one obtains

$$\langle E\rangle = \frac{5N}{2\beta} - \frac{NmgL}{\exp(\beta mgL) - 1}$$

and

$$c_V = \frac{R}{M}\left\{\frac{5}{2} - \left[\frac{\beta mgL}{\exp(\beta mgL) - 1}\right]^2 \exp(\beta mgL)\right\} .$$

Limiting cases: In an infinite cylinder or at a low temperature ($\beta mgL \to \infty$), one recovers $c_V = 5R/2M$, whereas in a short cylinder where gravity does not matter or at a high temperature ($\beta mgL \to 0$) one obtains $c_V = 3R/2M$ (Fig. 8.1).

We now extend the analysis by taking into account the decrease of gravitational acceleration with the distance from the center of the Earth $r$. In this case $g(r) = g_0(R_e/r)^2$, where $g_0$ denotes the gravitational acceleration at the surface of the Earth and $R_e$ the diameter of the Earth. The integral over the momenta remains unaltered as the variation of $g$ with $r$ only affects the integral over the spatial coordinates. The potential energy with a reference value of zero at $r \to \infty$ is equal to $\phi(r) = \int_{\infty}^{r} mg(r)\,\mathrm{d}r = -mg_0R_e^2/r$. Upon switching to spherical coordinates we have

$$\exp(-\beta F) \propto \left[4\pi \int_{R_e}^{\infty} \exp\left(\frac{\beta m g_0 R_e^2}{r}\right) r^2\,\mathrm{d}r\right]^N .$$

The above integral diverges at infinity. This indicates that the probability distribution $\rho(E)$ cannot be normalized in the usual manner because it is not sufficiently localized. At the same time we note that the potential energy is bounded from above and allows for unbounded states of atoms with positive energy. These can escape from the gravitational field of the Earth if their velocity exceeds the second cosmic escape velocity.

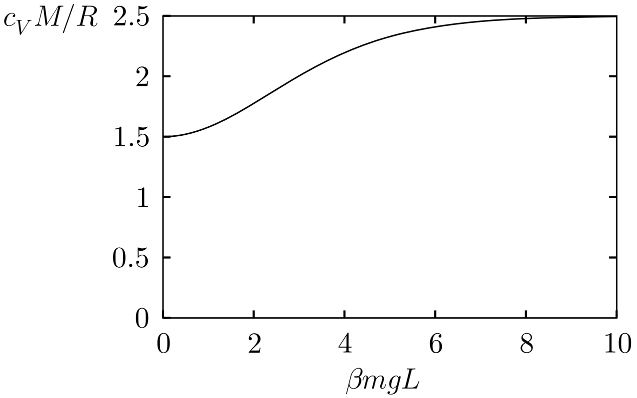

**Fig. 8.1** Heat capacity of an atom in an isothermal atmosphere of height $L$ and at a constant gravitational acceleration

**Problem 8.2.**

*A straight narrow tunnel is drilled through the center of a planet of mass and diameter of* $M = 2 \times 10^{28}$ kg *and* $R = 10^5$ km, *respectively. The tunnel is filled with argon at* 100 K. *The potential energy of an atom of mass m at a distance r from the center of the planet is given by* $GmMr^2/2R^3$, *where* $G = 6.67 \times 10^{-11}$ Nm$^2$/kg$^2$ *is the gravitational constant. Calculate* $\langle r\rangle$, $\langle r^2\rangle$, *and* $\sigma = (\langle r^2\rangle - \langle r\rangle^2)^{1/2}$ *for a single atom! The kilomolar mass of argon is* 40 kg/kmol.

We first introduce a shorthand $\alpha = \beta GmM/2R^3$. To evaluate the above averages, we need to calculate

$$\langle r^n\rangle = \frac{\int_0^R \exp(-\alpha r^2) r^n \mathrm{d}r}{\int_0^R \exp(-\alpha r^2)\mathrm{d}r}$$

for $n = 1$ and 2. We assume that most of the argon is localized near the center of the planet so that the upper bound of the integrals can be pushed towards infinity. Using $\int_0^\infty \exp(-\alpha r^2)\mathrm{d}r = \sqrt{\pi}/2\sqrt{\alpha}$, $\int_0^\infty \exp(-\alpha r^2) r \mathrm{d}r = 1/2\alpha$, as well as $\int_0^\infty \exp(-\alpha r^2) r^2 \mathrm{d}r = \sqrt{\pi}/4\alpha\sqrt{\alpha}$ one then obtains $\langle r\rangle = 1/\sqrt{\alpha\pi} = 99.4$ km, $\langle r^2\rangle = 1/2\alpha = 15520$ km$^2$, and $\sigma = (\langle r^2\rangle - \langle r\rangle^2)^{1/2} = 75.1$ km. As $\langle r\rangle \ll R$, the above assumption is justified. Note that $\langle r^2\rangle$ can also be obtained by applying the equipartition theorem for the potential energy $E_p$, which states that $\langle E_p\rangle = \alpha\langle r^2\rangle/\beta = k_B T/2$.

**Problem 8.3.**

*A sealed cylinder contains one kilogram of monatomic gas at* 20 °C. *The cylinder radius and height are* 35 cm *and* 1.5 m, *respectively. The cylinder rotates at a frequency of* 50 s$^{-1}$ *about its axis. The kilomolar mass of the gas is* 40 kg/kmol. *Calculate the heat capacity of the gas!*

In equilibrium established by collisions of atoms with the walls of the container walls and with each other, the gas rotates together with the container. In a rotating reference frame, a centrifugal force acts on the atoms and the corresponding centrifugal potential is $\phi(r) = -\int_0^r m\omega^2 r\,\mathrm{d}r = -m\omega^2 r^2/2$; $m$, $\omega$, and $r$ denote the mass of an atom, the angular velocity, and the distance from the axis, respectively. For each atom, the rotational contribution to the partition function reads

$$\exp\left(-\beta F_r\right) \propto \int_0^{R_c} \exp\left(\frac{\beta m\omega^2 r^2}{2}\right)\mathrm{d}\mathbf{r} = \frac{2\pi h}{\beta m\omega^2}\int_0^{\beta m\omega^2 R_c^2/2} \exp u \,\mathrm{d}u\,,$$

where $\mathrm{d}\mathbf{r} = 2\pi hr\,\mathrm{d}r$ and $u = \beta m\omega^2 r^2/2$; $R_c$ and $h$ denote the radius and the height of the cylinder, respectively. Thus the average energy of $N$ particles due to rotation

$$\langle E_r\rangle = N\left(\frac{\partial \beta F_r}{\partial \beta}\right)_V = N\left\{k_B T - \frac{m\omega^2 R_c^2 \exp\left(\beta m\omega^2 R_c^2/2\right)}{2\left[\exp\left(\beta m\omega^2 R_c^2/2\right) - 1\right]}\right\},$$

whereas the corresponding heat capacity is

$$c_V^r = \frac{R}{M}\left(1 - \left\{\frac{\beta m\omega^2 R_c^2}{2\left[\exp\left(\beta m\omega^2 R_c^2/2\right) - 1\right]}\right\}^2 \exp\left(\frac{\beta m\omega^2 R_c^2}{2}\right)\right).$$

Limiting cases: In case of slow rotation, small diameter of the cylinder, or high temperature where $\beta m\omega^2 R_c^2 \to 0$, we have $c_V^r = 0$; in the opposite case where $\beta m\omega^2 R_c^2 \to \infty$ we obtain $c_V^r = R/M$ as predicted by the equipartition theorem. With the given data, $c_V^r = 5.3 \times 10^{-7} R/M$ which can be neglected compared to the heat capacity due to translational motion $3R/2M \approx 311$ J/kgK.

**Problem 8.4.**
*An ideal gas held in a spherical container is exposed to an external potential* $\phi(r) = \phi_0 \ln\left(r/a\right)$, *where r is the distance from the center and* $a = 0.1$ m *is the radius of the container*; $\phi_0 = 0.05$ eV. *Calculate the heat capacity per molecule at* 20 °C*! What is the average distance of a molecule from the center of the container?*

The partition function for a single molecule in the above external potential is

$$\begin{aligned}\exp\left(-\beta F\right) &\propto \left[\int_{-\infty}^{\infty} \exp\left(-\frac{\beta p^2}{2m}\right)\,\mathrm{d}p\right]^3 4\pi\int_0^a \exp\Big(-\beta\phi_0 \ln\left(\frac{r}{a}\right)\Big) r^2\,\mathrm{d}r\\ &= \left(\frac{2\pi m}{\beta}\right)^{3/2} \frac{4\pi a^3}{3}\left(1 - \frac{\beta\phi_0}{3}\right)^{-1},\end{aligned}$$

where we took into account that $\exp\big(-\beta\phi_0 \ln(r/a)\big) = (r/a)^{-\beta\phi_0}$. The partition function converges only for $\beta < 3/\phi_0$, i.e., at temperatures above $T_p = \phi_0/3k_B$.

The average energy is $\langle E\rangle = k_B T_p\left[3T/2T_p - \left(1 - T_p/T\right)^{-1}\right]$, with the corresponding heat capacity at constant volume

$$C_V = k_B\left[\frac{3}{2} + \left(\frac{T}{T_p} - 1\right)^{-2}\right]$$

equal to $5.25\,k_B = 7.25 \times 10^{-23}$ J/K at 20 °C.

The average distance of the molecules from the center of the container reads

$$\langle r\rangle = \frac{\int_0^a (r/a)^{-\beta\phi_0}\, r^3\, \mathrm{d}r}{\int_0^a (r/a)^{-\beta\phi_0}\, r^2\, \mathrm{d}r} = a\frac{T/T_p - 1}{4T/3T_p - 1}\,,$$

which gives $0.505\,a = 5.05$ cm at 20 °C. The temperature dependence of $\langle r\rangle$ illustrates the behavior of the system at $T_p$: At this temperature, all molecules condense in the center of the container where the potential diverges, which in turn results in a diverging partition function (Fig. 8.2).

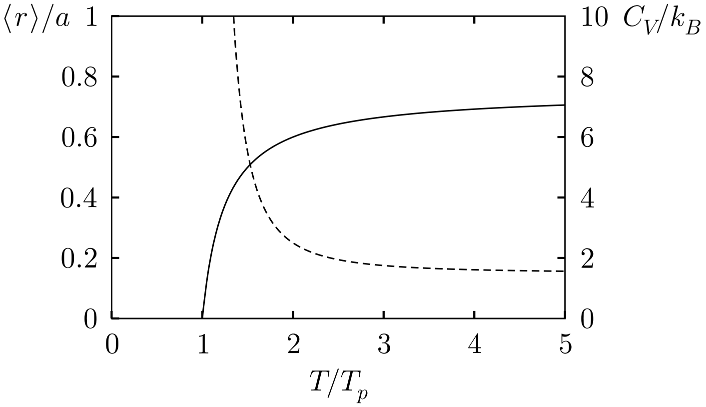

**Fig. 8.2** Average distance of molecules from the center of the logarithmic external potential (solid line) and the heat capacity (dashed line) plotted as a function of reduced temperature. At $T = T_p$, all molecules assemble at the center of the container where the potential diverges. At high temperatures the molecules behave as if there was no potential: The heat capacity tends to $3k_B/2$ and $\langle r\rangle$ approaches $3a/4$

## Problem 8.5.

*Write the partition function of an ideal monatomic gas at constant temperature and pressure! Calculate the average volume of such a gas as well as the magnitude of volume fluctuations!*

We start by considering the canonical isothermal–isochoric ensemble—a gas of $N$ particles in a box of volume $V_0$ at temperature $T$. The partition function reads

$$Z(N, V_0, T) = \frac{(2j+1)^N}{N!h^{3N}} \int \exp(-\beta E)\, \mathrm{d}^N\mathbf{p}\, \mathrm{d}^N\mathbf{r}\,.$$

The prefactor of $(2j+1)^N/N!h^{3N}$ results from the quasi-classical treatment; here $j$ denotes the angular momentum of each atom and $h = 6.626 \times 10^{-34}$ Js is the Planck constant. We introduce the reduced spatial coordinates $\mathbf{s}$ so that $\mathrm{d}\mathbf{r} = V_0\,\mathrm{d}\mathbf{s}$; thus

$$Z(N, V_0, T) = \frac{(2j+1)^N V_0^N}{N!h^{3N}} \int \exp(-\beta E)\, \mathrm{d}^N\mathbf{p}\, \mathrm{d}^N\mathbf{s}\,.$$

Now imagine a tiny cylinder with a freely moving piston located in the box (Fig. 8.3). We denote the number of atoms inside the cylinder by $M$; consequently, $N - M$ atoms remain in the box but outside the cylinder. We further assume that $M \ll N$.

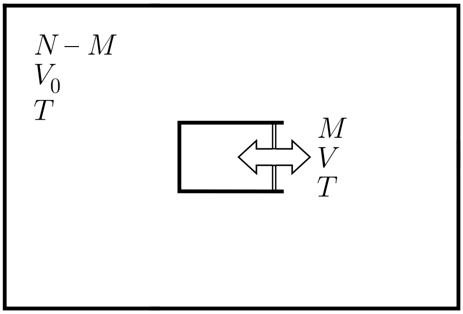

**Fig. 8.3** Box-and-cylinder arrangement used in the derivation of the partition function of the isothermal–isobaric ensemble

As before, the volume of the box is denoted by $V_0$ and the variable cylinder volume is $V$. The temperatures of gas in both subsystems are the same. The partition function of the whole system (i.e., the gas in the cylinder and the gas in the box) is equal to the product of the partition functions for the two subsystems, and volume $V$ is an additional variable in phase space, i.e., $Z \propto \int_V Z(M, V, T)Z(N - M, V_0 - V, T)\,\mathrm{d}V$. Then we have

$$\begin{aligned} Z \propto & \int_V \frac{(2j+1)^M V^M}{M! h^{3M}}\,\mathrm{d}V \int \exp\left(-\beta E_M\right) \mathrm{d}^M\mathbf{p}\,\mathrm{d}^M\mathbf{s} \\ & \times \frac{(2j+1)^{N-M}(V_0 - V)^{N-M}}{(N-M)! h^{3(N-M)}} \int \exp\left(-\beta E_{N-M}\right) \mathrm{d}^{N-M}\mathbf{p}\,\mathrm{d}^{N-M}\mathbf{s}\,, \end{aligned}$$

where $E_M$ and $E_{N-M}$ are the energies of the two subsystems. Since $V \ll V_0$ we can write

$$\left(1 - \frac{V}{V_0}\right)^{N-M} \approx \exp\left(-\frac{(N-M)V}{V_0}\right) = \exp\left(-\beta p V\right),$$

where we used the ideal gas equation of state $p = (N - M)k_B T/V_0$ for the gas inside the box (without the cylinder). Thus

$$\begin{aligned} Z \propto & \int_V \frac{(2j+1)^M V^M}{M! h^{3M}}\,\mathrm{d}V \int \exp\big(-\beta(E_M + pV)\big) \mathrm{d}^M\mathbf{p}\,\mathrm{d}^M\mathbf{s} \\ & \times \frac{(2j+1)^{N-M} V_0^{N-M}}{(N-M)! h^{3(N-M)}} \int \exp\left(-\beta E_{N-M}\right) \mathrm{d}^{N-M}\mathbf{p}\,\mathrm{d}^{N-M}\mathbf{s}\,. \end{aligned}$$

The second factor is independent of the variable cylinder volume $V$ and represents the phase integral $Z(N-M, V_0, T)$ of a gas of $N-M$ atoms contained in a box with constant volume $V_0$; $Z(N-M, V_0, T)$ does not involve the gas in the cylinder. From the first factor we deduce the partition function for a gas inside the cylinder subject to $p = const.$ and $T = const.$ which reads

$$Z(M, p, T) \propto \frac{(2j+1)^M}{M!h^{3M}} \int_V V^M \mathrm{d}V \int \exp\left(-\beta H_M\right) \mathrm{d}^M\mathbf{p}\, \mathrm{d}^M\mathbf{s}\,,$$

where $V$ acts as an additional phase-space coordinate. Note that now the argument of the Boltzmann factor contains enthalpy $H_M = E_M + pV$ rather than energy. The probability density for a $M$-particle system is

$$\rho_M \propto V^M \exp\left(-\beta H_M\right).$$

The ensemble defined by the probability density $\rho_M = \rho_M(T, p)$ is referred to as isothermal–isobaric.

In an ideal gas, the energy $E_M$ is of an entirely kinetic origin; the interactions between atoms are absent. After evaluating the integrals over linear momenta and over reduced coordinates, we are left with

$$Z(M, p, T) \propto \frac{(2j+1)^M}{M!h^{3M}} \left(\frac{2\pi m}{\beta}\right)^{3M/2} I_M\,,$$

where $m$ is the mass of each single atom and

$$I_M = \int_0^\infty V^M \exp\left(-\beta pV\right) \mathrm{d}V = \frac{M!}{(\beta p)^{M+1}}\,.$$

is integrated by parts in $M-1$ steps. Therefore the average volume of the gas is

$$\langle V\rangle = \frac{\int \mathrm{d}^M\mathbf{p}\, \mathrm{d}^M\mathbf{s} \int_V \rho_M V\, \mathrm{d}V}{\int \mathrm{d}^M\mathbf{p}\, \mathrm{d}^M\mathbf{s} \int_V \rho_M\, \mathrm{d}V} = \frac{I_{M+1}}{I_M} = \frac{M+1}{\beta p} \approx \frac{M}{\beta p}\,.$$

Here we rederived the ideal-gas equation of state $p = Mk_BT/\langle V\rangle$. On the other hand, the magnitude of volume fluctuations is quantified by $\sigma_V = \sqrt{\langle V^2\rangle - \langle V\rangle^2}$. In order to evaluate $\sigma_V$ we also need to calculate

$$\langle V^2\rangle = \frac{\int \mathrm{d}^M\mathbf{p}\, \mathrm{d}^M\mathbf{s} \int_V \rho_M V^2\, \mathrm{d}V}{\int \mathrm{d}^M\mathbf{p}\, \mathrm{d}^M\mathbf{s} \int_V \rho_M\, \mathrm{d}V} = \frac{I_{M+2}}{I_M} = \frac{(M+2)(M+1)}{(\beta p)^2}\,.$$

Thus $\sigma_V^2 = \langle V^2\rangle - \langle V\rangle^2 \approx M/(\beta p)^2$ and

$$\frac{\sigma_V}{\langle V\rangle} = \frac{1}{\sqrt{M}}\,.$$

In the thermodynamic limit where $M \to \infty$, volume fluctuations are negligible.

**Problem 8.6.**
*After the vapor of a nematogenic substance is exposed to a magnetic field of strength* $\mathbf{H}$, *the energy of each molecule changes by* $E(\mathbf{a}, \mathbf{H}) = -\gamma(\mathbf{a} \cdot \mathbf{H})^2$, *where* $\mathbf{a}$ *is the unit vector along the molecular long axis. Calculate the average and the fluctuations of* $E(\mathbf{a}, \mathbf{H})$ *of one liter of rarefied vapor at* $1\ \mathrm{mbar}$ *and* $300\ \mathrm{K}$ *with* $H = 10^6\ \mathrm{A/m}$ *and* $\gamma = 5 \times 10^{-35}\ \mathrm{Vsm^2/A}$*! What is the value of the nematic order parameter given by* $S = \langle [3(\mathbf{a} \cdot \mathbf{h})^2 - 1]/2 \rangle$*? Here* $\mathbf{h}$ *represents a unit vector directed along the magnetic field and* $\langle \cdots \rangle$ *stands for thermal averaging.*

In a rarefied vapor, molecules are independent from each other; therefore, the $N$-molecule magnetic contribution to the partition function can be written as

$$\exp(-\beta F) \propto \left[ \int_0^\pi \exp(\beta \gamma H^2 \cos^2\theta) 2\pi \sin\theta \, \mathrm{d}\theta \right]^N .$$

Here $\theta$ is the angle between the molecular long axis and the magnetic field so that $\cos\theta = \mathbf{a} \cdot \mathbf{h}$. Upon inserting the numerical data we find that $\beta\gamma H^2 \ll 1$ so that the exponent can be expanded in a Taylor series. In doing so, some care is needed because fluctuations of the magnetic energy involve the derivative $\left(\partial^2 \beta F / \partial \beta^2\right)_H$ and thus the partition function must be calculated exactly up to second order in $\beta$. We obtain

$$\exp(-\beta F) \propto \left[ \int_0^\pi \left( 1 + \beta\gamma H^2 \cos^2\theta + \frac{\beta^2 \gamma^2 H^4 \cos^4\theta}{2} \right) 2\pi \sin\theta \, \mathrm{d}\theta \right]^N$$
$$= \left[ 4\pi \left( 1 + \frac{\beta\gamma H^2}{3} + \frac{\beta^2\gamma^2 H^4}{10} \right) \right]^N .$$

To lowest order, the average magnetic energy is

$$\langle E_m \rangle = \left( \frac{\partial \beta F}{\partial \beta} \right)_H \approx -\frac{N\gamma H^2}{3} = -4.0 \times 10^{-4}\ \mathrm{J} .$$

Here the number of molecules is calculated using the ideal-gas equation of state: $N = pV/k_B T$. The square of energy fluctuations is given by

$$\sigma_E^2 = -\left( \frac{\partial^2 \beta F}{\partial \beta^2} \right)_H \approx \frac{4N\gamma^2 H^4}{45}$$

so that $\sigma_E \approx 2\sqrt{N}\gamma H^2 / 3\sqrt{5} = 7.3 \times 10^{-14}$ J. When evaluating the nematic order parameter, we recall that $\beta\gamma H^2 \ll 1$ and again stick to the lowest order expansion to find that

$$S = \frac{\int_0^\pi (3\cos^2\theta - 1) \exp(\beta\gamma H^2 \cos^2\theta) 2\pi \sin\theta \, \mathrm{d}\theta}{2 \int_0^\pi \exp(\beta\gamma H^2 \cos^2\theta) 2\pi \sin\theta \, \mathrm{d}\theta}$$

$$\approx \frac{2\beta\gamma H^2}{15} = 1.6 \times 10^{-3} \,.$$

**Problem 8.7.**
*The* 500 nm *gap between two parallel plates is filled by a dilute solution of tobacco mosaic virus (TMV). The virus is a thin rigid* 300 nm-*long rod. Calculate the nematic order parameter of the viruses! The order parameter is defined by* $S = \left\langle \left(3\cos^2\theta - 1\right)/2 \right\rangle$, *where* $\theta$ *is the angle between the plate normal and the long axis of the virus. Redo the calculation for the case where the gap between the plates is reduced to* 100 nm*!*

As far as the orientational order of the viruses is concerned, the relevant part of TMV phase space consists of the transverse coordinate $z$ (here measured from the center of the gap) and of the angle between the long axis and the normal of the plates denoted by $\theta$. If the gap width $h$ exceeds the length of the virus $d$, the orientation of viruses is unrestricted and $\theta$ can take any value between 0 and $\pi/2$. (NB: Due to the mirror symmetry of the viruses, angles between $\pi/2$ and $\pi$ correspond to the same physical states and hence considering these values would unnecessarily double the phase space.) The tilt determines the range of the allowed location of the center-of-mass reaching from $-z_\theta = -\left(h - d\cos\theta\right)/2$ to $z_\theta = \left(h - d\cos\theta\right)/2$. Here we spell out only the part of the partition function that affects $\langle\cos^2\theta\rangle$, which reads

$$\exp\bigl(-\beta F(h > d)\bigr) = \int_0^{\pi/2} \sin\theta\,\mathrm{d}\theta \int_{-z_\theta}^{z_\theta} \mathrm{d}z = h - \frac{d}{2}$$

and the average appearing in the nematic order parameter is

$$\left\langle\cos^2\theta\right\rangle = \exp\bigl(\beta F(h > d)\bigr) \int_0^{\pi/2} \cos^2\theta \sin\theta\,\mathrm{d}\theta \int_{-z_\theta}^{z_\theta} \mathrm{d}z = \frac{1}{3}\frac{h - 3d/4}{h - d/2} \,.$$

If the gap width is smaller than the length of viruses, $h < d$, the tilt must be larger than $\theta_{\mathrm{min}} = \arccos(h/d)$ and we obtain

$$\exp\bigl(-\beta F(h < d)\bigr) = \int_{\theta_{\mathrm{min}}}^{\pi/2} \sin\theta\,\mathrm{d}\theta \int_{-z_\theta}^{z_\theta} \mathrm{d}z = \frac{h^2}{2d}$$

and

$$\left\langle\cos^2\theta\right\rangle = \exp\bigl(\beta F(h < d)\bigr) \int_{\theta_{\mathrm{min}}}^{\pi/2} \cos^2\theta \sin\theta\,\mathrm{d}\theta \int_{-z_\theta}^{z_\theta} \mathrm{d}z = \frac{h^2}{6d^2} \,.$$

Consequently, the nematic order parameter is given by

$$S(h) = \begin{cases} \left(h^2/2d^2 - 1\right)/2, & h < d \\ \left(1 - 2h/d\right)^{-1}/4, & h > d \end{cases} .$$

As shown in Fig. 8.4, $S < 0$ for all gap widths $h$, indicating that on average the viruses orient perpendicular to the plate normal. In the limit of $h \to 0$, all viruses are forced to lie within the $xy$ plane and one has $S = -1/2$, whereas at $h/d \gg 1$ the orientation of the viruses is completely arbitrary with $S = 0$. —For $h = 500$ nm and 100 nm we have $S = -0.107$ and $-0.472$, respectively.

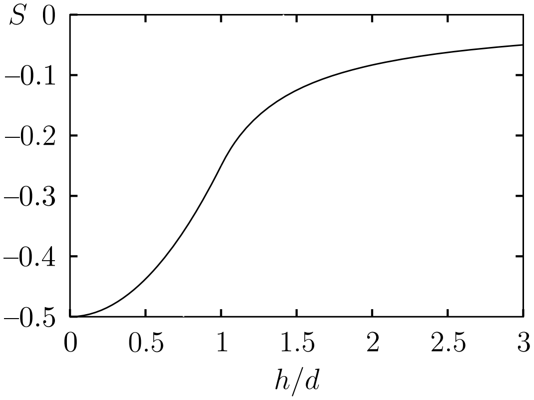

**Fig. 8.4** Nematic order parameter of a solution of tobacco mosaic virus confined to a gap between parallel plates vs. gap width. In a very thin gap, all rods lie flat between the plates and $S = -1/2$, whereas in a very thick gap which approaches a bulk ensemble we have $S \to 0$

## Problem 8.8.

*The elastic energy of a bond connecting two neighboring monomers in a polymer chain depends on the angle $\theta$ between the long axes of the monomers and reads $\phi(\theta) = -\phi_0 \cos\theta$. Because of steric interactions between the monomers, $\theta$ is restricted to values between* 0 *and* $\Theta$. *Compare the conformational heat capacity of a chain with $\Theta = 2\pi/3$ to that of a chain without steric restrictions! Temperature is* 20 °C *and* $\phi_0 = 0.05$ eV.

The state of a chain consisting of $N + 1$ monomers is specified by the $N$ independent bond angles (Fig. 8.5). We are interested only in the conformational part of the partition function given by

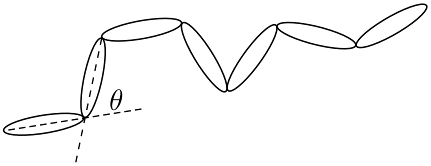

**Fig. 8.5** Polymer chain where the energy of the bond between nearest-neighbor monomers depends on angle $\theta$

$$\exp(-\beta F) = \left[\int_0^{\Theta} \exp(\beta\phi_0 \cos\theta) 2\pi \sin\theta \, \mathrm{d}\theta\right]^N$$
$$= \left\{2\pi(\beta\phi_0)^{-1}\left[\exp(\beta\phi_0) - \exp(\beta\phi_0 \cos\Theta)\right]\right\}^N .$$

The average intramolecular energy is equal to

$$\langle E\rangle = \frac{\mathrm{d}\beta F}{\mathrm{d}\beta} = N\left[\frac{1}{\beta} - \phi_0 \frac{\exp(\beta\phi_0) - \cos\Theta \exp(\beta\phi_0 \cos\Theta)}{\exp(\beta\phi_0) - \exp(\beta\phi_0 \cos\Theta)}\right]$$

and the heat capacity is

$$C = \frac{\mathrm{d}\langle E\rangle}{\mathrm{d}T} = Nk_B\left[1 - u(\beta\phi_0)^2\left(\frac{1-\cos\Theta}{1-u}\right)^2\right],$$

where $u = \exp\big(\beta\phi_0(\cos\Theta - 1)\big)$. For a chain without steric restrictions ($\Theta = \pi$) this gives $C = 0.69\, Nk_B$, whereas in a chain with restrictions the heat capacity is smaller; for $\Theta = 2\pi/3$, $C' = 0.50\, Nk_B$. The ratio of the two heat capacities is $C'/C = 0.72$.

**Problem 8.9.**
*Calculate the heat capacity of a polymer chain if the elastic energy of a bond between neighboring monomers is proportional to the angle between the long axes of the monomers, i.e.,* $\phi = \phi_0\theta$*! The chain consists of* 100 *monomers*, $\phi_0 = 0.05$ eV, *and temperature is* 20 °C.

Since $N$ bonds in a $N+1$-monomer chains are independent, the conformational part of the partition function reads

$$\exp(-\beta F) = \left[\int_0^{\pi} \exp(-\beta\phi_0\theta)\, 2\pi \sin\theta \, \mathrm{d}\theta\right]^N$$
$$= \left[2\pi\frac{1+\exp(-\pi\beta\phi_0)}{1+(\beta\phi_0)^2}\right]^N .$$

The average energy of the chain is

$$\langle E\rangle = \frac{\mathrm{d}\beta F}{\mathrm{d}\beta} = N\phi_0\left[\frac{\pi}{\exp(\pi\beta\phi_0)+1} + \frac{2\beta\phi_0}{1+(\beta\phi_0)^2}\right],$$

whereas the heat capacity plotted in Fig. 8.6 is

$$C = Nk_B\left\{\frac{\pi^2\exp(\pi\phi_0/k_BT)}{(k_BT/\phi_0)^2\left[\exp(\pi\phi_0/k_BT)+1\right]^2} + \frac{2\left[1-(k_BT/\phi_0)^2\right]}{\left[1+(k_BT/\phi_0)^2\right]^2}\right\}.$$

At $T = 0$, the heat capacity of a single bond would be equal to $2k_B$ (if, of course, the classical physics involved were applicable down to absolute zero), whereas at high temperatures it goes to 0. For a 100-monomer chain at 20 °C, $C = 1.40 \times 10^{-21}$ J/K.

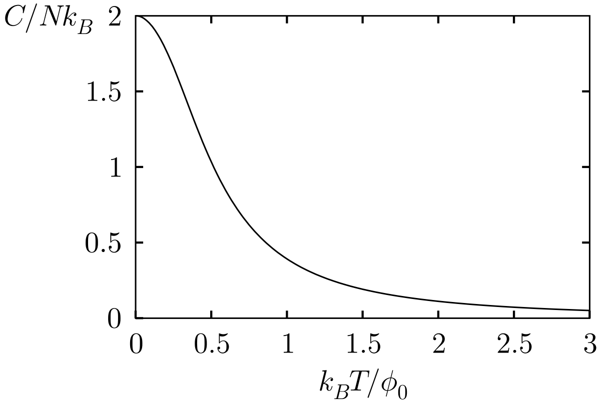

**Fig. 8.6** Heat capacity of a polymer chain where the bond energy is proportional to the angle between the long axes of neighboring monomers

**Problem 8.10.**

*Vinyl polymers can be represented by chains of identical elongated monomers, where each monomer forms a fixed angle with its neighbors but is free to rotate about the long axis of either neighbor. Calculate the persistence length*

$$\ell_p = \lim_{N\to\infty} \langle \mathbf{u}_1 \cdot \mathbf{r} \rangle$$

*of such a chain! Here N denotes the number of monomers in a chain,* $\mathbf{r}$ *is the vector connecting the chain ends,* $\mathbf{u}_1$ *is a unit vector defining the orientation of the monomer at the beginning of the chain, and* $\langle \cdots \rangle$ *stands for averaging over conformations. Calculate* $\langle r^2 \rangle$ *for a long vinyl chain! Finally, consider the limiting case of a perfectly flexible, freely jointed chain!*

The length of each monomer is denoted by $a$ and its orientation is described by a unit vector $\mathbf{u}_i$. As the angle between neighboring monomers is fixed, $\mathbf{u}_i \cdot \mathbf{u}_{i+1} = \cos\theta = const.$, whereas the rotation around $\mathbf{u}_i$ parametrized by the azimuthal angle $\phi_i$ is unhindered. In order to calculate the persistence length one must evaluate

$$\langle \mathbf{u}_1 \cdot \mathbf{r} \rangle = a \sum_{i=1}^{N} \langle \mathbf{u}_1 \cdot \mathbf{u}_i \rangle \ ,$$

where $\mathbf{r} = a \sum_{i=1}^{N} \mathbf{u}_i$. Similarly,

$$\left\langle r^2 \right\rangle = \langle \mathbf{r} \cdot \mathbf{r} \rangle = a^2 \sum_{i=1}^{N} \sum_{j=1}^{N} \left\langle \mathbf{u}_i \cdot \mathbf{u}_j \right\rangle = a^2 \left( N + \sum_{i \neq j} \langle \mathbf{u}_i \cdot \mathbf{u}_j \rangle \right).$$

In a freely jointed chain, all $\mathbf{u}_i$ are uncorrelated; hence $\langle \mathbf{u}_i \cdot \mathbf{u}_j \rangle = \delta_{ij}$. In this limit, the persistence length $\ell_p$ which represents a measure for chain stiffness is equal to the monomer length $a$: Orientational correlations between monomers do not even reach to the nearest neighbors. At the same time, we also find that $\langle r^2 \rangle = Na^2$—a well-known result from diffusion in three dimensions.

In a vinyl chain that is not fully flexible, the orientations of two monomers are correlated, with $\langle \mathbf{u}_i \cdot \mathbf{u}_j \rangle \neq 0$ even for $i \neq j$. Consider two neighboring monomers at sites $i$ and $i + 1$. In addition to the vector $\mathbf{u}_i$ we also define the vectors $\mathbf{v}_i$ and $\mathbf{w}_i$ so as to construct an orthonormal triad fixed to the section of the chain just before site $i + 1$. One can write

$$\mathbf{u}_{i+1} = \cos\theta\, \mathbf{u}_i + \sin\theta \cos\phi_i\, \mathbf{v}_i + \sin\theta \sin\phi_i\, \mathbf{w}_i$$

and analogously

$$\mathbf{u}_{i+2} = \cos\theta\, \mathbf{u}_{i+1} + \sin\theta \cos\phi_{i+1}\, \mathbf{v}_{i+1} + \sin\theta \sin\phi_{i+1}\, \mathbf{w}_{i+1}\,.$$

Now we calculate $\langle \mathbf{u}_i \cdot \mathbf{u}_{i+2} \rangle$. When averaging over the azimuthal angles $\phi_i$ and $\phi_{i+1}$, we take into account that the monomers can rotate freely around the long axes of their neighbors, and thus the Boltzmann factor does not depend on these two angles. In this case one is left with $\langle \mathbf{u}_i \cdot \mathbf{u}_{i+2} \rangle = \cos^2\theta$ alone. By repeating the above procedure one realizes that in general

$$\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k} \rangle = \cos^k\theta = \nu^k\,.$$

The magnitude of this result decreases with increasing $k$, indicating that with increasing inter-monomer distance the orientational correlations become weaker and weaker. Here we introduced $\cos\theta = \nu$.

The persistence length is thus equal to

$$\ell_p = \lim_{N\to\infty} a \sum_{i=1}^{N} \langle \mathbf{u}_1 \cdot \mathbf{u}_i \rangle = \lim_{N\to\infty} a \sum_{k=0}^{N-1} \langle \mathbf{u}_1 \cdot \mathbf{u}_{k+1} \rangle = a \sum_{k=0}^{\infty} \nu^k = \frac{a}{1-\nu}\,.$$

In the last step, we recognized that the terms to be summed constitute an infinite geometric series. In a fully stretched-out chain where $\theta = 0$ and $\nu = 1$, $\ell_p$ diverges.

The average $\langle r^2 \rangle$ can be recast as

$$\begin{aligned}\left\langle r^2 \right\rangle &= a^2 \left[ N + 2 \sum_{k=1}^{N-1} (N-k)\nu^k \right] \\ &= a^2 \left[ N + 2 \frac{\nu(\nu^N - 1) + N\nu(1-\nu)}{(1-\nu)^2} \right].\end{aligned}$$

(The above sum was evaluated by taking the derivative of the geometric series $\sum_k \nu^k$ with respect to $\nu$.) For a very long chain ($N \to \infty$) one has

$$\left\langle r^2 \right\rangle = Na^2 \frac{1+\nu}{1-\nu} .$$

In a "tetrahedral" chain with $\theta = 70.5°$ ($\nu = 0.3338$) we obtain $\langle r^2 \rangle = 2.002\, Na^2$ (which is approximately twice as much as for the freely jointed chain), the corresponding persistence length being $1.501\, a$.

## Problem 8.11.

*Calculate the persistence length and the average square of the chain end-to-end distance for a long Langevin chain! In a Langevin chain, the energy of the bond connecting the neighboring monomers is given by $\phi(\theta) = -\phi_0 \cos\theta$, where $\theta$ is the angle between their long axes. The temperature is* 300 K *and* $\phi_0 = 0.05$ eV.

The persistence length $\ell_p$ and the average square chain end-to-end distance $\langle r^2 \rangle$ are calculated by following the same steps as in Problem 8.10. We first reevaluate the average of the dot product $\mathbf{u}_i \cdot \mathbf{u}_{i+k}$. After averaging over azimuthal angles, some terms vanish like in Problem 8.10 and we are left with the averages over the independent polar angles $\theta_i$:

$$\begin{aligned}\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k} \rangle &= \left\langle \prod_{j=0}^{k-1} \cos\theta_{i+j} \right\rangle = \prod_{j=0}^{k-1} \left\langle \cos\theta_{i+j} \right\rangle \\ &= \left[ \frac{\int_{-1}^{1} \exp\left(\beta\phi_0 \cos\theta_i\right) \cos\theta_i \, \mathrm{d}\cos\theta_i}{\int_{-1}^{1} \exp\left(\beta\phi_0 \cos\theta_i\right) \mathrm{d}\cos\theta_i} \right]^k \\ &= \left( \coth\beta\phi_0 - \frac{1}{\beta\phi_0} \right)^k .\end{aligned}$$

Now we denote $\coth\beta\phi_0 - 1/\beta\phi_0$ by $\nu$ and immediately use the expressions for $\ell_p$ and $\left\langle r^2 \right\rangle$ derived in Problem 8.10. At high temperatures one has $\beta\phi_0 \to 0$ and thus $\nu \to 0$ so that the chain behaves as if it were freely jointed despite the nonzero conformational energy: $\ell_p$ amounts to one monomer length. In the low-temperature limit ($\beta\phi_0 \to \infty$, $\nu \to 1$) the chain is fully extended and $\ell_p$ diverges. At 300 K we obtain $\ell_p = 2.11\, a$ and $\left\langle r^2 \right\rangle = 3.21\, Na^2$.

## Problem 8.12.

*In an alkane chain, a quartet of four consecutive carbon atoms can bond in three different ways:* trans ($t$), gauche+ ($g^+$), *or* gauche− ($g^-$). *The two* gauche *bonding energies are identical and exceed the* trans *bonding energy by* 0.025 eV. *For steric reasons, the "neighboring" quartets which share three consecutive carbon atoms cannot appear in conformations* $g^+g^-$ and $g^-g^+$.

*Calculate the partition function for the conformations of an n-pentane molecule*

$$\underbrace{\mathrm{CH_3} - \mathrlap{\overbrace{\phantom{\mathrm{CH_2} - \mathrm{CH_2} - \mathrm{CH_2} - \mathrm{CH_3}}}^{\text{quartet}}}\mathrm{CH_2} - \mathrm{CH_2} - \mathrm{CH_2}}_{\text{quartet}} - \mathrm{CH_3} \quad !$$

*At what temperature do* 55% *of the molecules contain exactly one quartet in the* trans *conformation on average? Estimate the fluctuations of the conformational energy in one liter of gaseous n-pentane at this temperature and a pressure of* 1 bar*!*

Some of the *n*-pentane conformations are shown in Fig. 8.7. We set the conformational energies of each carbon atom quartet in the *trans* ($t$) and *gauche* ($g^+$, $g^-$) conformations to 0 and $w > 0$, respectively.

**Fig. 8.7** Some of the conformations of *n*-pentane. From left to right: $tt$, $tg^-$, and the "prohibited" $g^+g^-$. The gray rods represent the carbon chain, whereas the protruding rods shown in white correspond to hydrogen atoms

The energies of all possible conformations of the *n*-pentane molecule are listed in the table below:

| Conformation | $t\,t$ | $t\,g^+$ | $t\,g^-$ | $g^+\,t$ | $g^-\,t$ | $g^+\,g^+$ | $g^-\,g^-$ |
|---|---|---|---|---|---|---|---|
| Energy | 0 | $w$ | $w$ | $w$ | $w$ | $2w$ | $2w$ |

The conformational contribution to the partition function of a *n*-pentane chain is given by

$$\exp(-\beta F) = 1 + 4\exp(-\beta w) + 2\exp(-2\beta w)\,.$$

There are four conformations featuring exactly one *trans* carbon atom quartet ($tg^+$, $tg^-$, $g^+t$, and $g^-t$), and the probability of such bonding is

$$P = \frac{4\exp(-\beta w)}{1 + 4\exp(-\beta w) + 2\exp(-2\beta w)} = \frac{4u}{1 + 4u + 2u^2}\,.$$

Here $u = \exp(-\beta w)$. To find the temperature where $P = 0.55$, one has to solve a quadratic equation $2Pu^2 + 4(P-1)u + P = 0$. The physically relevant solution is $u_0 = 0.407$, yielding $T = -w/k_B \ln u_0 = 322$ K.

For one molecule, the magnitude of fluctuations of the conformational energy is obtained from

$$\sigma_E^2 = -\frac{\mathrm{d}^2\beta F}{\mathrm{d}\beta^2} = 4w^2\frac{u_0\left(1+2u_0+2u_0^2\right)}{\left(1+4u_0+2u_0^2\right)^2}\,.$$

For $N = pV/k_BT$ molecules in a gaseous sample confined to volume $V$ at pressure $p$ one has

$$(\sigma_E)_N = \sigma_E\sqrt{N} = 9.45\times10^{10}w = 2.36\times10^9\ \mathrm{eV}\,.$$

## Problem 8.13.

*In a simple model of thermal expansion of solids, one assumes that the atoms can be regarded as independent one-dimensional anharmonic oscillators in a potential given by $\phi(x) = ax^2 - bx^3 + cx^4$. How does the average position of such an oscillator depend on temperature in the range where $b\langle x^3\rangle \ll k_BT$ and $c\langle x^4\rangle \ll k_BT$? Calculate the linear thermal expansion coefficient of such a solid! Apply the result to a diatomic molecule where the atoms are bound by the Lennard-Jones potential $\phi(r) = \phi_0\left[(r/r_0)^{-12} - 2(r/r_0)^{-6}\right]$! Assume that the temperature is low enough so that $\phi_0 \gg k_BT$ yet high enough so that classical mechanics still applies.*

We seek $\langle x\rangle = \int_{-\infty}^{\infty} x\exp\left(-\beta\phi(x)\right)\mathrm{d}x/\int_{-\infty}^{\infty}\exp\left(-\beta\phi(x)\right)\mathrm{d}x$. Because of the smallness of the anharmonic terms in the potential, the exponential factor $\exp\left(\beta(bx^3-cx^4)\right)$ appearing in the integrands can be expanded into $1+\beta(bx^3-cx^4)$, thereby simplifying the algebra:

$$\langle x\rangle = \frac{\int_{-\infty}^{\infty}\exp(-\beta ax^2)\left[x+\beta(bx^4-cx^5)\right]\mathrm{d}x}{\int_{-\infty}^{\infty}\exp(-\beta ax^2)\left[1+\beta(bx^3-cx^4)\right]\mathrm{d}x}$$

$$= \frac{\int_0^{\infty}\exp(-\beta ax^2)\beta bx^4\,\mathrm{d}x}{\int_0^{\infty}\exp(-\beta ax^2)(1-\beta cx^4)\,\mathrm{d}x}\,.$$

Note that the odd terms in the integrands do not contribute as the integration interval is symmetric. Upon inserting $\int_0^{\infty}x^{2n}\exp(-\beta ax^2)\,\mathrm{d}x = (2n-1)!!\sqrt{\pi}/2^{n+1}(\beta a)^{n+1/2}$, we find that to the lowest order

$$\langle x\rangle \approx \frac{3bk_BT}{4a^2}\,.$$

Thus the linear thermal expansion coefficient is equal to

$$\alpha = \frac{1}{\ell}\frac{\mathrm{d}\ell}{\mathrm{d}T} = \frac{1}{\ell}\frac{\mathrm{d}\langle x\rangle}{\mathrm{d}T} = \frac{3bk_B}{4a^2\ell},$$

where $\ell$ denotes the equilibrium distance between neighboring atoms. One can see that thermal expansion cannot be described with a harmonic potential ($b = c = 0$) since in this case $\alpha = 0$.

The result can also be used to study the expansion of a diatomic molecule. The Lennard-Jones potential has a minimum at $r = r_0$, and at low enough temperatures the equilibrium atom-to-atom distance does not depart significantly from $r_0$. In this regime the potential can be Taylor-expanded around $r = r_0$, yielding

$$\phi(r \approx r_0) = \phi_0 \left( -1 + \frac{36}{r_0^2}x^2 - \frac{252}{r_0^3}x^3 + \frac{1113}{r_0^4}x^4 + \ldots \right),$$

where $x = r - r_0$ (Fig. 8.8). From here we now extract the coefficients $a$, $b$, and $c$. By taking $\ell = r_0$, we finally have

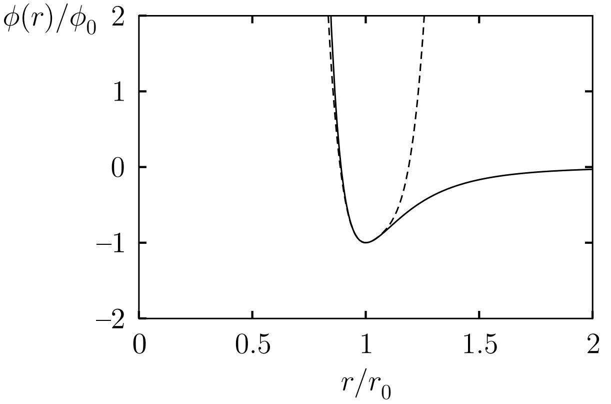

**Fig. 8.8** Lennard-Jones potential (solid line) is repulsive for $r < r_0$ and attractive for $r > r_0$. Close to the minimum it can be approximated by a fourth-order polynomial (dashed line)

$$\alpha \approx \frac{7k_B}{48\phi_0}.$$

It turns out that the partition function calculated for a particle in a Lennard-Jones potential does not converge, whereas the partition function for the anharmonic potential does exist. This apparent contradiction is resolved as follows: In this Problem, we are interested in the thermal expansion of a diatomic molecule, which is a bonded state of one atom in the potential of the other by definition, and not in the behavior of free atoms. As the atoms are bonded, the interatom distance never differs significantly from its equilibrium value and thus it is plausible to replace the exact dependence $\phi(r)$ by a fourth-order polynomial.

### Problem 8.14.

*A sensitive spring balance contains a spring of stiffness of* $10^{-2}$ N/m. *Estimate the smallest mass that can be still weighed using such a balance at* 300 K*!*

The theoretical sensitivity of a balance is determined by the thermal fluctuations of spring extension. The elastic energy of the spring is equal to $E = Kx^2/2$, where $x$ is extension and $K$ is the stiffness of the spring. The mass $m$ to be weighed and the extension $x$ are related by Hooke's law $Kx = mg$, where $g$ is the gravitational acceleration. From the equipartition theorem one has $\langle E\rangle = K\langle x^2\rangle/2 = k_BT/2$, which can be used to estimate the amplitude of extension fluctuations $\sqrt{\langle x^2\rangle} = \sqrt{k_BT/K}$. Thus

$$m \approx \frac{K\sqrt{\langle x^2\rangle}}{g} = \frac{\sqrt{Kk_BT}}{g} = 6.4 \times 10^{-13}\,\mathrm{kg}\,.$$

**Problem 8.15.**

*One end of a freely jointed polymer chain consisting of* $10^6$ *monomers of non-negligible mass is anchored to a long rigid rod. Calculate the average height of the center of mass measured relative to the anchored end as well as its fluctuations at* 300 K*! The length of each monomer is* 5 nm *and the kilomolar mass of the monomer is* 3200 kg/kmol. *Disregard any interaction between the supporting rod and the chain.*

The potential energy of the polymer consisting of $N$ monomers is $E = \sum_{j=1}^{N} mgl_j$, where $m$ is the monomer mass, $g$ is the gravitational acceleration, and $l_j$ is the vertical coordinate of $j$-th monomer relative to the anchored end. The average vertical coordinate of the center of mass of the polymer is located at

$$\langle z^*\rangle = \frac{\sum_{j=1}^{N} l_j}{N} = \frac{\langle E\rangle}{Nmg},$$

which implies that $\langle z^*\rangle$ can be obtained from the average potential energy $\langle E\rangle$. We parametrize the orientation of a given monomer by the polar angle $\theta_j$ between the long axis of the monomer and the $z$ axis, and the azimuthal angle, which is irrelevant in the present context. The vertical coordinate of the $j$-th monomer depends on the orientation of all monomers between the anchored end and itself, and is given by $l_j = a\big(\sum_{i=1}^{j-1}\cos\theta_i + \cos\theta_j/2\big)$, where $a$ is the monomer length. After rearranging the terms we have

$$E = mga\sum_{j=1}^{N}\left(N + \frac{1}{2} - j\right)\cos\theta_j\,.$$

The relevant part of the partition function then reads

$$\exp\left(-\beta F\right) \propto \int_0^{\pi}\cdots\int_0^{\pi}\exp\left(-\alpha\sum_{j=1}^{N}\left(N + \frac{1}{2} - j\right)\cos\theta_j\right)\prod_{j=1}^{N}\sin\theta_j \mathrm{d}\theta_j\,.$$

where we introduced $\alpha = \beta mga$. Although the location of a given monomer does depend on the location of the monomers that connect it to the anchored end (and thus the system is not ideal as it does not consist of independent particles), the partition function can still be factorized. After integrating over all $\theta_j$ one obtains

$$\exp(-\beta F) \propto \prod_{j=1}^{N} \frac{2\sinh\big(\alpha(N+1/2-j)\big)}{\alpha(N+1/2-j)}$$
$$\approx 2^N \prod_{j=1}^{N}\left[1+\frac{\alpha^2}{6}\left(N+\frac{1}{2}-j\right)^2\right].$$

Here we took into account that $N\alpha \ll 1$; the system is in the high-temperature limit. Apart from an irrelevant additive constant,

$$\beta F = -\frac{\alpha^2}{6}\left[N\left(N+\frac{1}{2}\right)^2 - 2\left(N+\frac{1}{2}\right)\sum_{j=1}^{N} j + \sum_{j=1}^{N} j^2\right].$$

After evaluating the two sums we find that

$$\beta F = -\frac{(\beta m g a)^2}{72}\big(4N^2-1\big)N$$

and thus

$$\langle z^*\rangle = \frac{\langle E\rangle}{Nmg} = \frac{1}{Nmg}\frac{\mathrm{d}\beta F}{\mathrm{d}\beta} = -\frac{\beta m g a^2}{36}\big(4N^2-1\big) = -36\,\mathrm{nm}.$$

The center of mass of the polymer is thus slightly below the anchored end. Note that it scales approximately as $N^2$ rather than with $N$, which is a signature of the nonideal nature of the system. If gravity were switched off ($g = 0$), $\langle z^*\rangle = 0$ as expected. The fluctuations of the vertical position of the center of mass are given by

$$\sigma_{z^*} = \frac{1}{Nmg}\sqrt{-\frac{\mathrm{d}\langle E\rangle}{\mathrm{d}\beta}} = \frac{a}{6}\sqrt{\frac{4N^2-1}{N}} = 1.7\,\mu\mathrm{m}.$$

As $\sigma_{z^*} \gg |\langle z^*\rangle|$, the state of the polymer chain is largely unaffected by gravity, which is anticipated since $N\alpha \ll 1$.

# Chapter 9
# Equation of State

**Problem 9.1.**
*The electric dipole moment of a water molecule is equal to* $6.1 \times 10^{-30}$ Asm. *Calculate the electric susceptibility of saturated water vapor at* $100\,^\circ\mathrm{C}$*! Analyze the behavior of polarization fluctuations!*

In absence of an external electric field, the orientational distribution of water molecules is isotropic; therefore the macroscopic electric polarization of the sample vanishes. In an external field **E**, on the other hand, the dipoles on average align along the field which gives rise to an electric polarization $P = n\langle \mathbf{p}_e \cdot \mathbf{E}/E\rangle = n\langle p_e \cos\theta\rangle$ (Fig. 9.1); here $\mathbf{p}_e$ is the dipole moment of each molecule, $n$ is the number density of the molecules, and $\theta$ is the angle between a dipole and the field. The energy of a dipole in the external field is equal to $-\mathbf{p}_e \cdot \mathbf{E} = -p_e E \cos\theta$. The average $\langle p_e \cos\theta\rangle$ only depends on the orientational degrees of freedom, and given the uniaxial symmetry of the problem with respect to **E** the infinitesimal element of the phase space of interest is $2\pi \sin\theta\, d\theta$. In vapor at low densities, interactions between the dipoles can

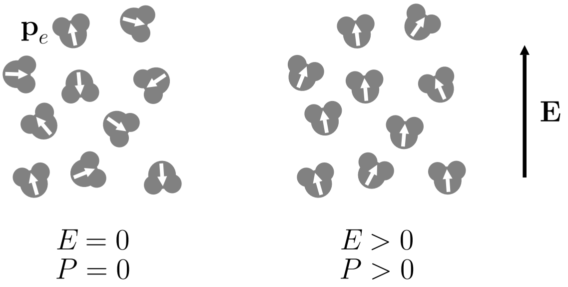

**Fig. 9.1** Electric dipole moment of water molecules points along the twofold axis from the oxygen atom toward the midpoint between the hydrogen atoms. In absence of an external field, the dipoles in vapor are orientationally disordered and the overall polarization of the sample is 0. After the field is switched on, the dipoles partly align along the field which results in a nonzero net polarization

G. Skačej and P. Ziherl, *Solved Problems in Thermodynamics and Statistical Physics*, https://doi.org/10.1007/978-3-030-27661-4_9

be neglected and we have

$$\langle p_e \cos\theta \rangle = p_e \frac{\int_0^\pi \cos\theta \exp\left(\beta p_e E \cos\theta\right) 2\pi \sin\theta \, \mathrm{d}\theta}{\int_0^\pi \exp\left(\beta p_e E \cos\theta\right) 2\pi \sin\theta \, \mathrm{d}\theta} = p_e L\left(\frac{p_e E}{k_B T}\right),$$

where we introduced the Langevin function

$$L(u) = \coth u - \frac{1}{u}$$

plotted in Fig. 9.2. The same result can also be obtained by evaluating the partition function

$$\begin{aligned} \exp\left(-\beta F_e\right) &\propto \left[\int_0^\pi \exp\left(\beta p_e E \cos\theta\right) 2\pi \sin\theta \, \mathrm{d}\theta\right]^N \\ &= \left[4\pi \frac{\sinh(\beta p_e E)}{\beta p_e E}\right]^N \end{aligned}$$

(here written for $N$ molecules), taking its logarithm, and then calculating the derivative of $\beta F_e$ with respect to $\beta E$. Thus we directly obtain $N \langle p_e \cos\theta \rangle$.

When talking about electric susceptibility $\chi$, one usually thinks of weak electric fields where polarization is proportional to field strength: $P = \chi \epsilon_0 E$. In the $E \to 0$ limit one can expand the Langevin function $\coth u - 1/u \approx u/3$, so that the induced polarization is equal to $P = n p_e^2 E / 3 k_B T$. This is the Curie law with the characteristic temperature dependence $\chi \propto 1/T$. The particle density can now be expressed from the ideal gas equation of state $p_s = n k_B T$, where $p_s$ is the saturated vapor pressure

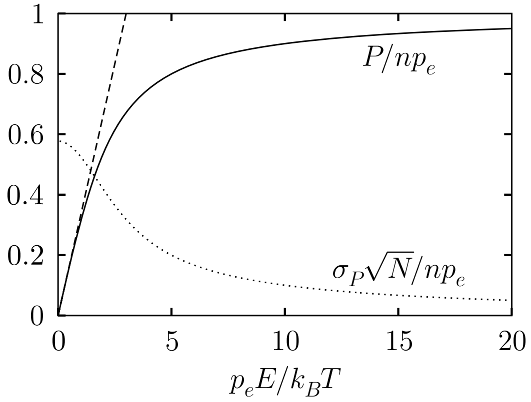

**Fig. 9.2** Polarization of an ideal gas consisting of molecules that carry electric dipoles (solid line) and polarization fluctuations (dotted line) as a function of the reduced electric field strength $p_e E / k_B T$; $P/n p_e$ coincides with the Langevin function $L(u) = \coth u - 1/u$. The limiting behavior of the polarization in a weak field or, alternatively, at a high temperature, is given by the Curie law (dashed line)

at 100 °C ($\approx$ 1 bar). We obtain

$$\chi = \frac{p_e^2 p_s}{3\epsilon_0 k_B^2 T^2} = 5.3 \times 10^{-3}\,.$$

The amplitude of polarization fluctuations around the average is calculated as follows:

$$\begin{aligned}\sigma_P^2 = \langle P^2\rangle - \langle P\rangle^2 &= -\frac{1}{V^2}\left(\frac{\partial^2 \beta F_e}{\partial(\beta E)^2}\right)_V = \frac{1}{V}\left(\frac{\partial\langle P\rangle}{\partial \beta E}\right)_V \\ &= N\left(\frac{k_B T}{EV}\right)^2\left\{1-\left[\frac{p_e E/k_B T}{\sinh(p_e E/k_B T)}\right]^2\right\}.\end{aligned}$$

At high temperatures or in a weak field where $k_B T/p_e E \gg 1$, $\sigma_P$ approaches $np_e/\sqrt{3N}$, whereas at low temperatures, we have $\sigma_P \approx nk_B T/E\sqrt{N}$ (Fig. 9.2). In both cases fluctuations are negligible in the thermodynamic limit.

**Problem 9.2.**
*Analyze the high- and the low-temperature behavior of the orientational contribution to the heat capacity in a system of independent electric dipoles in an external electric field!*

The average energy $-\langle p_e \cos\theta\rangle E$ is readily obtained from the result for $\langle p_e \cos\theta\rangle$ derived in Problem 9.1. The heat capacity per dipole is then equal to

$$C = k_B\left[1-\left(\frac{p_e E}{k_B T}\right)^2 \sinh^{-2}\left(\frac{p_e E}{k_B T}\right)\right].$$

At low temperatures we have—again assuming that classical physics applies down to absolute zero—

$$C \approx k_B\left[1-4\left(\frac{p_e E}{k_B T}\right)^2 \exp\left(-\frac{2p_e E}{k_B T}\right)\right] \to k_B\,,$$

whereas at high temperatures

$$C \approx \frac{k_B}{3}\left(\frac{p_e E}{k_B T}\right)^2 \to 0\,.$$

The high-temperature result is easy to interpret: In this limit, all orientations of the dipoles are equiprobable, and a further increase of internal energy by heating is not possible.

**Problem 9.3.**
*At* 20 °C, *the relative permittivity of liquid water is equal to* 80 *and mainly originates in the permanent electric dipoles of the molecules. Calculate the value of the dipole*

*moment by including the dipole–dipole interaction represented by the local field* $E_{\mathrm{loc}} = E + P/3\epsilon_0$, *where* $E$ *is the strength of the external field and* $P$ *is polarization!*

The average component of the dipole along the external field is calculated in Problem 9.1. We use this result, substitute $E$ by the local field $E_{\mathrm{loc}}$, and expand the Langevin function around zero. This gives

$$P \approx \frac{np_e^2 E_{\mathrm{loc}}}{3k_B T} = \frac{np_e^2}{3k_B T}\left(E + \frac{P}{3\epsilon_0}\right),$$

where $n$ is the number density of the molecules. Thus

$$P = \frac{3a}{1-a}\epsilon_0 E\,,$$

where $a$ stands for $np_e^2/9k_B T\epsilon_0$. Evidently, $3a/(1-a)$ represents the electric susceptibility $\chi = \epsilon - 1$ so that $a = (\epsilon - 1)/(\epsilon + 2)$. Thus we derived the Clausius–Mossotti formula

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{np_e^2}{9k_B T\epsilon_0}$$

which states that at a constant temperature, the ratio $(\epsilon - 1)/(\epsilon + 2)$ is proportional to the density of matter. The electric dipole moment of the water molecule obtained using this model with $\epsilon = 80$ is equal to $3.06 \times 10^{-30}$ Asm, which is approximately one half of the correct value.

**Problem 9.4.**

*Explore the ferroelectric–paraelectric transition in the mean-field approximation where one assumes that each dipole is exposed to a local field* $E_{\mathrm{loc}} = P/3\epsilon_0$, $P$ *being the electric polarization!*

We use the results obtained in Problem 9.1, replacing the external electric field $E$ in the result for polarization by the local field $E_{\mathrm{loc}}$. This gives an equation of state that determines the temperature dependence of the spontaneous polarization:

$$P_s = np_e\left(\coth\frac{p_e P_s}{3k_B T\epsilon_0} - \frac{3k_B T\epsilon_0}{p_e P_s}\right).$$

Here, $n$ is the number density of dipoles, $p_e$ is the dipole moment, and $T$ is the temperature. For convenience, we introduce the reduced polarization $\mathcal{P}_s = P_s/np_e$ and temperature $\mathcal{T} = T/T_c$ with $T_c = np_e^2/9k_B\epsilon_0$. In terms of reduced variables, the equation of state reads

$$\mathcal{P}_s = \coth\frac{3\mathcal{P}_s}{\mathcal{T}} - \frac{\mathcal{T}}{3\mathcal{P}_s}\,.$$

Close to the phase transition we have $\mathcal{P}_s \ll 1$. By Taylor-expanding $\coth(u) \approx 1/u + u/3 - u^3/45 + \ldots$, we find that $\mathcal{P}_s \approx \mathcal{P}_s/\mathcal{T} - 3\mathcal{P}_s^3/5\mathcal{T}^3$ so that

$$\mathcal{P}_s \approx \sqrt{\frac{5}{3}\mathcal{T}^2\left(1 - \mathcal{T}\right)}\,.$$

The ferroelectric–paraelectric transition occurs at $\mathcal{T} = 1$; above this temperature the spontaneous polarization vanishes. One can notice that the model predicts the same critical exponent of the order parameter as the Landau theory of phase transitions.

The mean-field approximation can be applied at an arbitrary temperature. At low temperatures, we can replace coth $(3\mathcal{P}_s/\mathcal{T})$ by 1 which gives

$$\mathcal{P}_s \approx 1 - \frac{\mathcal{T}}{3} - \frac{\mathcal{T}^2}{9}.$$

As shown by Fig. 9.3, both approximations agree well with the exact solution $\mathcal{P}_s(\mathcal{T})$ in their respective regimes of applicability.

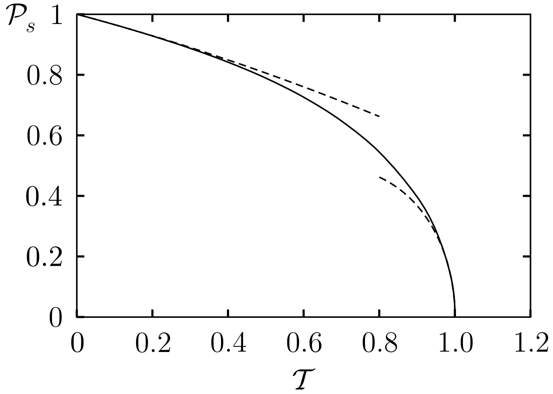

**Fig. 9.3** Spontaneous polarization of a ferroelectric predicted by mean-field approximation (solid line) vs. reduced temperature. Also plotted are the approximations valid at low temperatures and close to the ferroelectric–paraelectric transition (dashed lines). At low temperatures, $\mathcal{P}_s$ is an approximately linear function of $\mathcal{T}$, whereas close to the transition we observe a critical behavior characterized by the classical exponent $\beta = 1/2$

## Problem 9.5.

*Analyze the temperature dependence of electric susceptibility of a ferroelectric material in the mean-field approximation discussed in Problem 9.4!*

In an external electric field of strength $E$, a ferroelectric material is characterized by both spontaneous and induced polarization. The reduced form of the thus generalized equation of state (Problem 9.4) reads

$$\mathcal{P} = \coth \frac{3(\mathcal{P} + \mathcal{E})}{\mathcal{T}} - \frac{\mathcal{T}}{3(\mathcal{P} + \mathcal{E})},$$

where

$$\mathcal{P} = \mathcal{P}_s(\mathcal{T}) + \mathcal{P}_i$$

is the sum of reduced spontaneous and induced polarization and $\mathcal{E} = 3\epsilon_0 E/np_e$ is the reduced strength of the external electric field. In case where $\mathcal{P}_i \ll 1$ we obtain a linear relation between $\mathcal{P}_i$ and $\mathcal{E}$; the reduced susceptibility is then given by

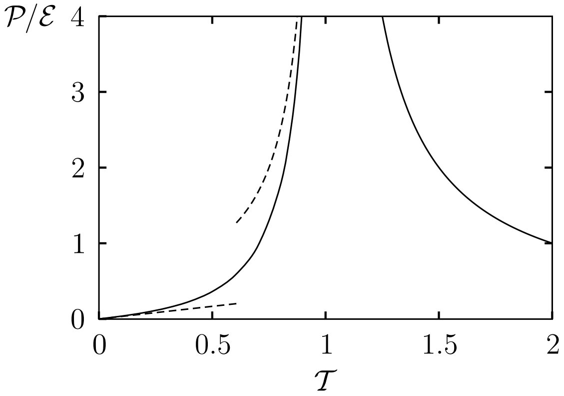

**Fig. 9.4** Reduced electric susceptibility of a ferroelectric material in mean-field approximation (solid line) and the approximate temperature dependences of the susceptibility in the ferroelectric phase (dashed lines). The predicted critical behavior agrees with the Landau theory of phase transitions

$$\frac{\mathcal{P}_i}{\mathcal{E}} = \frac{9\mathcal{P}_s^2\left[1-\coth^2\left(3\mathcal{P}_s/\mathcal{T}\right)\right]+\mathcal{T}^2}{3\mathcal{T}\mathcal{P}_s^2-9\mathcal{P}_s^2\left[1-\coth^2\left(3\mathcal{P}_s/\mathcal{T}\right)\right]-\mathcal{T}^2}\,.$$

Now we insert the approximate analytical expressions for $\mathcal{P}_s(\mathcal{T})$ obtained in Problem 9.4. In the ferroelectric phase at $\mathcal{T} \to 0$ we obtain $\mathcal{P}_i \approx \mathcal{T}\mathcal{E}/3$ so that to lowest order

$$\chi \approx \frac{9\epsilon_0 k_B T}{np_e^2}\,,$$

whereas just below the transition from the ferroelectric to the paraelectric phase $\mathcal{P}_i \approx \mathcal{E}/2\,(1-\mathcal{T})$ and so

$$\chi \approx \frac{np_e^2}{6\epsilon_0 k_B (T_c - T)}\,.$$

In the paraelectric phase we have $\mathcal{P}_i \approx \mathcal{E}/\left(\mathcal{T}-1\right)$ for all $\mathcal{T} > 1$ which gives

$$\chi \approx \frac{np_e^2}{3\epsilon_0 k_B (T - T_c)}\,.$$

In contrast with the expressions for the susceptibility of the ferroelectric phase which are approximate (although in good agreement with the numerical solution shown in Fig. 9.4), this result is exact since the spontaneous polarization of the paraelectric is equal to 0.

### Problem 9.6.

*Using the mean-field approximation, discuss the temperature dependence of the difference of heat capacities of the ferroelectric and paraelectric phase! Calculate the critical exponent $\alpha$!*

The average energy of a ferroelectric material is $\langle E\rangle = -V\mathbf{P}_s \cdot \mathbf{E}_{\text{loc}}/2$, where $V$ is the volume, $\mathbf{P}_s$ is the spontaneous polarization, and $\mathbf{E}_{\text{loc}}$ is the strength of the local electric field; the factor of $1/2$ originates from the pairwise nature of the dipole–dipole interactions. In the mean-field approximation, $\mathbf{E}_{\text{loc}} = \mathbf{P}_s/3\epsilon_0$. We introduce the reduced spontaneous polarization $\mathcal{P}_s = P_s/np_e$, where $n$ is the number density of the molecules, and we obtain

$$\langle E\rangle = -\frac{n^2 p_e^2 V}{6\epsilon_0}\mathcal{P}_s^2\,.$$

The heat capacities of the ferroelectric and the paraelectric phase differ by $\Delta c = (1/m)\mathrm{d}\langle E\rangle/\mathrm{d}T$, and at low temperatures we have

$$\frac{\Delta c}{c_0} \approx \frac{2}{3}\left(1 + \frac{\mathcal{T}}{3}\right),$$

where $c_0 = 3nk_B/2\rho$; $\rho$ is the density. On the other hand, close to the ferroelectric–paraelectric transition

$$\frac{\Delta c}{c_0} \approx \frac{5}{3}\mathcal{T}\,(3\mathcal{T} - 2)\,.$$

As seen in Fig. 9.5, the low-temperature approximation closely approaches the exact difference of heat capacities. On the other hand, just below the phase transition the agreement is not so good due to all of the simplifications, despite the correct magnitude of the jump at the transition. Note that $\Delta c$ is proportional to the derivative of the polarization which is not captured well by the approximate expressions used close to the transition.

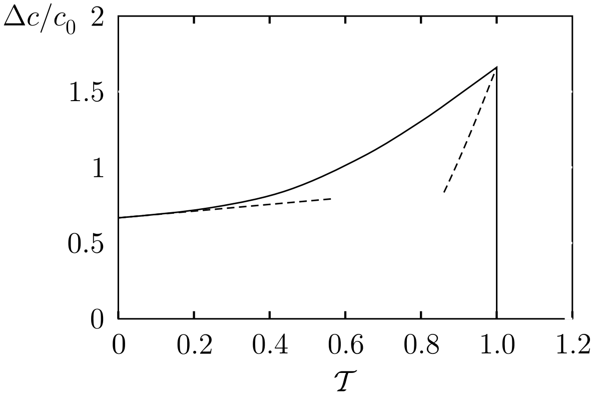

**Fig. 9.5** Reduced difference of heat capacities of the ferroelectric and the paraelectric phase in the mean-field approximation; here the agreement of approximate solutions (dashed lines) and the exact solution (solid line) is worse than in the spontaneous polarization and susceptibility. The critical exponent $\alpha$ is equal to 0: At the transition, $\Delta c$ exhibits a jump but does not diverge

**Problem 9.7.**
*How does the polarization at the ferroelectric–paraelectric transition depend on the strength of the external electric field within the mean-field approximation?*

Like in Problem 9.5, the equilibrium value of electric polarization is determined by the equation $\mathcal{P} = \coth\big(3(\mathcal{P}+\mathcal{E})/\mathcal{T}\big) - \mathcal{T}/3\,(\mathcal{P}+\mathcal{E})$. We expand the right-hand side for small $\mathcal{P}+\mathcal{E}$ and we take into account that at the transition $\mathcal{T}=1$. This gives

$$\mathcal{E} - \frac{3}{5}\,(\mathcal{P}+\mathcal{E})^3 = 0$$

and thus

$$\mathcal{P} = \left(\frac{5\mathcal{E}}{3}\right)^{1/3} - \mathcal{E} \approx \left(\frac{5\mathcal{E}}{3}\right)^{1/3}.$$

In the final step, we neglected the $\mathcal{E}$ term because it is subdominant for $\mathcal{E}\to 0$. The corresponding critical exponent $\delta$ is hence equal to 3, again in agreement with the Landau theory.

**Problem 9.8.**
*Two freely rotating electric dipoles are fixed at a separation of* $a = 20$ nm. *The dipole directions are determined by the unit vectors* $\mathbf{p}_1$ *and* $\mathbf{p}_2$. *The dipole–dipole interaction energy is given by*

$$\phi(\mathbf{p}_1,\mathbf{p}_2,\mathbf{a}) = \frac{\gamma}{a^3}\left[\mathbf{p}_1\cdot\mathbf{p}_2 - \frac{3}{a^2}(\mathbf{p}_1\cdot\mathbf{a})(\mathbf{p}_2\cdot\mathbf{a})\right],$$

*where* $\mathbf{a}$ *is a unit vector pointing from one suspension point to the other and* $\gamma = 6\times 10^{-46}$ Jm$^3$. *Calculate the average dipole–dipole interaction energy at* 300 K *where* $\gamma/a^3k_BT \ll 1$*! What is the force between the dipoles? How do the average energy and the force depend on the separation* $a$*?*

The orientation of each dipole is parametrized by the polar angle $\theta_i$ measured with respect to $\mathbf{a} = a(0,0,1)$ and by the azimuthal angle $\phi_i$ $(i = 1,2)$: $\mathbf{p}_i = (\sin\theta_i\cos\phi_i, \sin\theta_i\sin\phi_i, \cos\theta_i)$. The partition function reads

$$\begin{aligned}\exp(-\beta F) \propto &\int_0^{2\pi} \mathrm{d}\phi_1 \int_0^{\pi} \sin\theta_1\,\mathrm{d}\theta_1 \\ &\times \int_0^{2\pi} \mathrm{d}\phi_2 \int_0^{\pi} \exp\big(-\beta\phi(\mathbf{p}_1,\mathbf{p}_2,\mathbf{a})\big)\sin\theta_2\,\mathrm{d}\theta_2\,,\end{aligned}$$

where

$$\beta\phi(\mathbf{p}_1,\mathbf{p}_2,\mathbf{a}) = \frac{\beta\gamma}{a^3}\Big[\sin\theta_1\sin\theta_2\cos(\phi_1-\phi_2) - 2\cos\theta_1\cos\theta_2\Big].$$

In the high-temperature limit where $\beta\gamma/a^3 \ll 1$, the exponential function in the partition function should be expanded up to second order since the linear term vanishes upon integration. Once all integrals are calculated one obtains $\exp(-\beta F) \propto (4\pi)^2\left(1+\beta^2\gamma^2/3a^6\right)$: With the given data and to the lowest order, the average energy of the dipole interaction is

$$\langle E_d \rangle = \left(\frac{\partial \beta F}{\partial \beta}\right)_a \approx -\frac{2\gamma^2}{3k_B T a^6} = -5.6 \times 10^{-6}\ \mathrm{eV}\,.$$

On average, the dipole–dipole interaction is attractive and decreases rapidly with distance: $\langle E_d \rangle \propto a^{-6}$. The magnitude of the interaction decreases with increasing temperature. It is largest at low temperatures where the dipoles are mostly parallel to each other, but as the temperature is increased the orientation of the dipoles is more and more uncorrelated which leads to a weakening of the interaction. The force between the dipoles is

$$\mathcal{F} = -\left(\frac{\partial F}{\partial a}\right)_\beta \approx -\frac{2\gamma^2}{k_B T a^7} = -1.36 \times 10^{-16}\ \mathrm{N}$$

and decreases with distance as $\mathcal{F} \propto 1/a^7$.

**Problem 9.9.**
*Assume that a uniform electric field gradient can be established between two parallel plates* 1 m *apart so that the electric field strength is* 0 V/m *at the first plate and* $2 \times 10^7$ V/m *at the second one. The gap between the plates is filled with water vapor at a low density. Calculate the relative difference of the vapor densities next to the plates at* 400 K*! The electric dipole moment of the water molecule is* $6.1 \times 10^{-30}$ Asm. *Where is the center-of-mass plane of vapor and what is its average polarization? The number density of water molecules per unit plate area is* $1.8 \times 10^{25}/\mathrm{m}^2$.

In an inhomogeneous electric field, an electric dipole (representing a water molecule) is drawn in the direction of increasing field strength if it is parallel to the field and in the opposite direction if it is antiparallel to the field, which causes a repositioning of molecules within the gap. We denote the coordinate normal to the plates by $z$ such that $z = 0$ and $z = d$ correspond to the first and the second plate, respectively. Let $\theta$ denote the polar angle between the electric dipole moment $\mathbf{p}_e$ and the $z$ axis, and $|\mathrm{d}E_z/\mathrm{d}z|$ be the magnitude of the field gradient. In the parallel-plate geometry, a force of magnitude $\mathcal{F} = p_e \cos\theta\, |\mathrm{d}E_z/\mathrm{d}z|$ acts on a dipole along the $z$ axis. If we use the plate at $z = 0$ as a reference, the corresponding orientational-positional term in the Hamiltonian is given by $E(z,\theta) = -\int_0^z \mathcal{F}\mathrm{d}z = -p_e|\mathrm{d}E_z/\mathrm{d}z| z\cos\theta$. The resulting canonical probability density reads $\rho(z,\theta) = C\exp\left(\beta p_e |\mathrm{d}E_z/\mathrm{d}z| z\cos\theta\right)$, where $C$ is a constant. As far as the mass redistribution is concerned, one needs to consider the density of molecules as a function of $z$, and molecular orientation is irrelevant. Thus we project $\rho(z,\theta)$ onto the $z$-coordinate:

$$\rho(z) = \int_\Omega \rho(z,\theta)\,\mathrm{d}\phi\,\mathrm{d}(\cos\theta) = 4\pi C\frac{\sinh(\alpha z)}{\alpha z},$$

where $\alpha = \beta p_e |\mathrm{d}E_z/\mathrm{d}z|$. Given that $\alpha d \approx 0.022 \ll 1$, one can expand $\sinh x \approx x + x^3/6$. Then, the relative difference of vapor densities next to the plates is $[\rho(d) - \rho(0)]/\rho(0) \approx \alpha^2 d^2/6 = 8.1 \times 10^{-5}$. The center-of-mass plane is located at

$$z^* = \langle z \rangle = \frac{\int_0^d z\rho(z)\mathrm{d}z}{\int_0^d \rho(z)\mathrm{d}z} \approx \frac{d}{2}\left[1 + \frac{(\alpha d)^2}{36}\right],$$

which is only slightly displaced from the mid-plane (i.e., the zero-gradient position); the shift amounts to 6.8 $\mu$m. The average polarization is proportional to

$$\langle \cos\theta \rangle = \frac{\int_0^d \mathrm{d}z \int_{-1}^1 \mathrm{d}(\cos\theta)\rho(z,\theta)\cos\theta}{\int_0^d \mathrm{d}z \int_{-1}^1 \mathrm{d}(\cos\theta)\rho(z,\theta)} \approx \frac{\alpha d}{6}\left[1 - \frac{(\alpha d)^2}{180}\right],$$

where the integration over $\theta$ was performed by parts and the resulting hyperbolic functions were expanded up to third order. We define the polarization by $P = (N/Ad)p_e\langle\cos\theta\rangle$, where $A$ is the surface area of either plate, and obtain $P \approx 4 \times 10^{-7}$ As/m$^2$.

**Problem 9.10.**
*A keratin molecule (found in, e.g., wool fibers) can be represented by a chain of identical elongated segments. Consider a simple model where the segments can be oriented either along the chain or perpendicular to it and are assumed to be independent. The contribution of each segment to the chain energy depends on its orientation with respect to the chain. Calculate the average length, energy, and enthalpy of a chain subjected to a stretching force, and estimate the length fluctuations!*

We denote the length and the width of a segment by $a$ and $d$, respectively (Fig. 9.6). The energies of a lengthwise and a transverse segment are $E_a$ and $E_d$, respectively. We consider a keratin chain containing a total of $N$ segments, with $N_a$ in the lengthwise orientation and $N_d = N - N_a$ in the transverse orientation. The phase space consists of all possible arrangements of lengthwise and transverse segments. Note that in this system an intensive quantity (the force $\mathcal{F}$) rather than an extensive one (length $\ell$) is fixed. As a consequence, the probability density is a function of enthalpy $H = E - \mathcal{F}\ell$ rather than of the energy $E$ alone: $\rho(H) \propto \exp(-\beta H)$. (This is also discussed

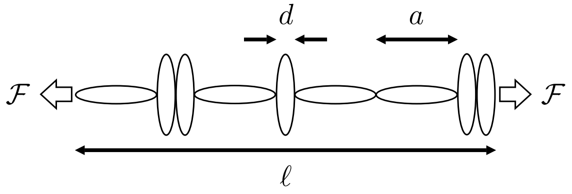

**Fig. 9.6** Model of a keratin molecule where only lengthwise and transverse orientations of the segments with respect to the chain are allowed; the molecule is stretched by a force $\mathcal{F}$

in Problem 8.5, where we examine an ideal gas at constant pressure rather than at constant volume.) In a stretched molecule, the more probable configurations include those with a low energy as well as those with the lengthwise orientation of the segments. Both length and energy of a given configuration depend on the number of transverse segments: $\ell(N_a) = aN_a + d(N - N_a)$ and $E(N_a) = E_a N_a + E_d(N - N_a)$. We now write the partition function (here represented by a sum rather than by an integral)

$$\exp(-\beta G) = \sum_{N_a=0}^{N} C(N, N_a) \exp\left(-\beta\big[E(N_a) - \mathcal{F}\ell(N_a)\big]\right),$$

where $G$ is the Gibbs free energy;

$$C(N, N_a) = \frac{N!}{N_a!(N - N_a)!} = \binom{N}{N_a}$$

denotes the number of different configurations with $N_a$ lengthwise segments and $N - N_a$ transverse segments (Fig. 9.7). Thus the partition function can be recast as

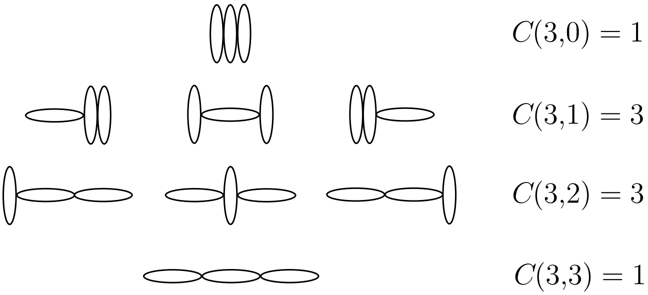

**Fig. 9.7** Possible configurations of a three-segment keratin molecule, with $\sum_{i=0}^{3} C(3, i) = 1 + 3 + 3 + 1 = 2^3$ possible arrangements

$$\exp(-\beta G) = \sum_{N_a=0}^{N} \binom{N}{N_a} \left[\exp\left(-\beta(E_a - \mathcal{F}a)\right)\right]^{N_a} \times \left[\exp\left(-\beta(E_d - \mathcal{F}d)\right)\right]^{N-N_a},$$

and after applying the binomial theorem one obtains

$$\exp(-\beta G) = \left[\exp\left(-\beta(E_a - \mathcal{F}a)\right) + \exp\left(-\beta(E_d - \mathcal{F}d)\right)\right]^{N}.$$

We see that the $N$-segment partition function has split into a product of partition functions for individual segments. This is expected because we assume that the segments are independent from each other. (An analogous result also follows if there exist more than two possible states of the segments.)

The average length of a keratin molecule is $\langle \ell \rangle = -\,(\partial\beta G/\partial\beta\mathcal{F})_\beta$ or

$$\begin{aligned}\langle \ell \rangle &= N\frac{a\exp\big(-\beta(E_a-\mathcal{F}a)\big)+d\exp\big(-\beta(E_d-\mathcal{F}d)\big)}{\exp\big(-\beta(E_a-\mathcal{F}a)\big)+\exp\big(-\beta(E_d-\mathcal{F}d)\big)}\\ &= a\langle N_a\rangle + d\langle N_d\rangle\,,\end{aligned}$$

where $\langle N_a\rangle$ and $\langle N_d\rangle$ are the average numbers of lengthwise and transverse segments, respectively. If the applied force is weak ($\beta\mathcal{F}a \ll 1$ and $\beta\mathcal{F}d \ll 1$), we have

$$\langle \ell \rangle = N\left\{\frac{d+a\exp\Delta}{1+\exp\Delta}+\beta\mathcal{F}\left[\frac{d^2+a^2\exp\Delta}{1+\exp\Delta}-\left(\frac{d+a\exp\Delta}{1+\exp\Delta}\right)^2\right]\right\},$$

where $\Delta = \beta(E_d - E_a)$. The first term in the curly bracket represents the average length of an unloaded molecule, whereas the second term is a correction due to the external force. The correction is a linear function of the force and is thus consistent with Hooke's law. If the applied force is large so that $\mathcal{F}a \gg E_a$ and $\mathcal{F}d \gg E_d$, then

$$\langle \ell \rangle = N\frac{d+a\exp\big(\beta\mathcal{F}(a-d)\big)}{1+\exp\big(\beta\mathcal{F}(a-d)\big)} \approx Na\,.$$

In this regime the molecule is fully stretched. (Here we assume that $a > d$.)

The amplitude of length fluctuations is described by

$$\begin{aligned}\sigma_\ell^2 = \langle \ell^2\rangle - \langle \ell\rangle^2 &= -\left(\frac{\partial^2\beta G}{\partial(\beta\mathcal{F})^2}\right)_\beta = \left(\frac{\partial\langle \ell\rangle}{\partial\beta\mathcal{F}}\right)_\beta\\ &= N(a-d)^2\frac{\exp\big(-\beta\big[E_a+E_d-\mathcal{F}(a+d)\big]\big)}{\big[\exp\big(-\beta(E_a-\mathcal{F}a)\big)+\exp\big(-\beta(E_d-\mathcal{F}d)\big)\big]^2}\,.\end{aligned}$$

We see that $\sigma_\ell^2$ is proportional to the difference $(a-d)^2$: If the length and the width of the segments are the same, the length of the molecule does not fluctuate.

The average energy and enthalpy are given by

$$\langle E\rangle = \left(\frac{\partial\beta G}{\partial\beta}\right)_{\beta\mathcal{F}} = E_a\langle N_a\rangle + E_d\langle N_d\rangle$$

and

$$\langle H\rangle = \left(\frac{\partial\beta G}{\partial\beta}\right)_{\mathcal{F}} = (E_a-\mathcal{F}a)\langle N_a\rangle + (E_d-\mathcal{F}d)\langle N_d\rangle\,,$$

respectively.

**Problem 9.11.**

*A polymer chain consists of* 20 *elongated monomers of length of* 2 nm *and width of* 1 nm, *each with an embedded longitudinal electric dipole moment of* $10^{-28}$ Asm. *If a monomer is parallel to the chain, its energy is* 0.08 eV, *whereas if it is perpendicular* *to the chain, its energy is* 0.1 eV. *Calculate the average chain length at* 20 °C*! By how much does the chain length change after an electric field of strength of* $5 \times 10^7$ V/m *is applied along the chain? Assume that the monomers' long axes lie in the same plane and that the dipoles are independent!*

The phase space of each monomer consists of four states because in both the lengthwise and the transverse orientation the dipole may point in two directions. Let us denote the two transverse states by $A$ and $B$ and the two lengthwise ones by $C$ and $D$. In state $C$ the dipole points along the electric field $\mathbf{E}$, whereas in state $D$ it points in the opposite direction (Fig. 9.8). The bonding energy of states $A$ and $B$ is $E_A = 0.1$ eV and that of states $C$ and $D$ is $E_C = 0.08$ eV. The width and length of the segment are denoted by $a$ and $c$, respectively. The partition function for a $N$-segment chain then reads

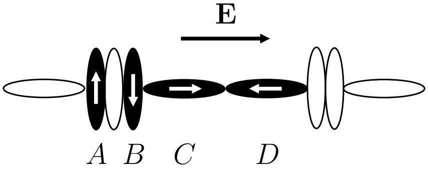

**Fig. 9.8** Possible bonding arrangements of polar monomers in a polymer chain. The four possible states are denoted by $A$, $B$, $C$, and $D$. The white arrow indicates the orientation of the electric dipole

$$\exp(-\beta G) = \big[2\exp(-\beta E_A) + \exp\big(-\beta(E_C - p_e E)\big) \\ + \exp\big(-\beta(E_C + p_e E)\big)\big]^N ,$$

where we have assumed that the chain segments are independent (Problem 9.10) and we used $p_e$ to denote the dipole moment of the segments. The average chain length is equal to

$$\langle \ell \rangle = a\big(\langle N_A\rangle + \langle N_B\rangle\big) + c\big(\langle N_C\rangle + \langle N_D\rangle\big) ,$$

where $\langle N_i\rangle$ ($i = A, B, C, D$) stands for the average number of segments in a given state. After introducing $\Delta = E_C - E_A$ and $z = 2\big[1 + \exp(-\beta\Delta)\cosh\beta p_e E\big]$, we have

$$\begin{aligned} \langle N_A\rangle &= N\exp(\beta G_1)\exp(-\beta E_A) = Nz^{-1}, \\ \langle N_B\rangle &= \langle N_A\rangle , \\ \langle N_C\rangle &= N\exp(\beta G_1)\exp\big(-\beta(E_C - p_e E)\big) \\ &= Nz^{-1}\exp\big(-\beta(\Delta - p_e E)\big), \\ \langle N_D\rangle &= N\exp(\beta G_1)\exp\big(-\beta(E_C + p_e E)\big) \\ &= Nz^{-1}\exp\big(-\beta(\Delta + p_e E)\big), \end{aligned}$$

where $\exp(-\beta G_1) = \exp(-\beta G/N)$ is the partition function for a single segment. In absence of the electric field the energy of the states $C$ and $D$ is degenerate and thus $\langle N_C\rangle = \langle N_D\rangle$. In this case the average length of a 20-segment chain equals $\langle \ell \rangle = 33.8$ nm. The electric field breaks the symmetry of the states $C$ and $D$ as more dipoles align parallel to the field than in the opposite direction. A field of strength of $5 \times 10^7$ V/m leads to a chain elongation of 2.3 nm.

**Problem 9.12.**

*A macromolecule can be modeled by a freely jointed polymer chain consisting of* 1 nm*-long rigid segments. Calculate the linear thermal expansion coefficient and the isothermal Young's modulus of such a chain at* 300 K *subjected to a stretching force of* 1 pN*! Examine the limits of weak and strong force!*

We denote the number of segments by $N$ and segment length by $a$. The orientation of each segment with respect to the chain end-to-end vector is given by the polar angle $\theta_i$, where $i = 1, \dots N$. The corresponding azimuthal angles are irrelevant as the chain length $\ell = \sum_{i=1}^{N} a\cos\theta_i$ does not depend on them. Like in Problem 9.10 the Boltzmann factor features the enthalpy $-\mathcal{F}\ell$, where $\mathcal{F}$ is the stretching force. (As the chain is freely jointed, the conformational energy is zero.) We obtain

$$\begin{aligned}\langle \ell \rangle &= Na\langle\cos\theta_i\rangle = Na\frac{\int_0^\pi \cos\theta_i \exp\left(\beta\mathcal{F}a\cos\theta_i\right)2\pi\sin\theta_i \,\mathrm{d}\theta_i}{\int_0^\pi \exp\left(\beta\mathcal{F}a\cos\theta_i\right)2\pi\sin\theta_i\,\mathrm{d}\theta_i}\\ &= Na\left(\coth\beta\mathcal{F}a - \frac{1}{\beta\mathcal{F}a}\right).\end{aligned}$$

This result formally coincides with the expression for the polarization of an ideal gas consisting of electric dipoles (Problem 9.1). In the weak-force regime where $\beta\mathcal{F}a \ll 1$, we obtain Hooke's law $\langle \ell \rangle \approx Na^2\mathcal{F}/3k_BT$, whereas in the strong-force regime where $\beta\mathcal{F}a \gg 1$ we have $\langle \ell \rangle \approx Na$. The linear thermal expansion coefficient is equal to

$$\begin{aligned}\alpha &= \frac{1}{\langle \ell \rangle}\left(\frac{\partial\langle \ell \rangle}{\partial T}\right)_{\mathcal{F}} = -\frac{1}{T}\frac{(\beta\mathcal{F}a)^{-1} - \beta\mathcal{F}a\sinh^{-2}(\beta\mathcal{F}a)}{\coth(\beta\mathcal{F}a) - (\beta\mathcal{F}a)^{-1}}\\ &= -0.0033\ \mathrm{K}^{-1}\end{aligned}$$

and is negative. The reciprocal isothermal Young's modulus reads

$$\begin{aligned}E_T^{-1} &= \frac{1}{\langle \ell \rangle}\left(\frac{\partial\langle \ell \rangle}{\partial \mathcal{F}}\right)_T = \beta a\frac{(\beta\mathcal{F}a)^{-2} - \sinh^{-2}(\beta\mathcal{F}a)}{\coth(\beta\mathcal{F}a) - (\beta\mathcal{F}a)^{-1}}\\ &= 9.9 \times 10^{11}\ \mathrm{N}^{-1}.\end{aligned}$$

Consequently, $E_T = 1.01$ pN. In the weak-force regime where Hooke's law is valid, we obtain $\alpha \approx -1/T$ and $E_T \approx \mathcal{F}$ (Fig. 9.9). On the other hand, if the force is very

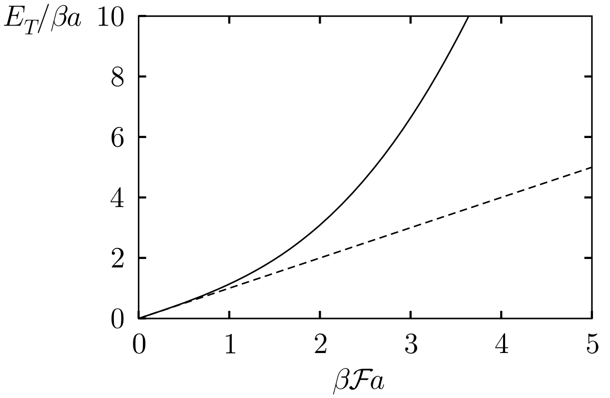

**Fig. 9.9** Isothermal Young's modulus of a freely jointed polymer (solid line), with Hooke's law $E_T = \mathcal{F}$ observed in the weak-force regime (dashed line)

strong ($\beta\mathcal{F}a \to \infty$) the macromolecule is fully stretched: In this regime one has $\alpha \to 0$, whereas $E_T$ diverges. We notice that $\alpha$ is negative, i.e., the macromolecule contracts upon heating. This can be understood by recalling that in the freely jointed polymers, the origin of elasticity is entirely entropic. Upon heating, the average orientational order of the chain stretched by a given force is decreased and the coil becomes more spherical. Thus the chain end-to-end distance decreases too.

**Problem 9.13.**

*Starting from a given pair potential $\phi(r)$, derive the equation of state for a nonideal monatomic gas at intermediate densities! Consider only pair interactions between the atoms and neglect clusters of more than two atoms.*

In order to derive the equation of state for a gas, $p = -(\partial F/\partial V)_\beta$, we begin with the Helmholtz free energy obtained by taking the logarithm of the partition function. The energy of a $N$-atom ensemble consists of the kinetic and the interaction term:

$$E = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i<j} \phi(r_{ij}) \,.$$

Here $m$ is the mass of a single atom, $p_i$ is the magnitude of the linear momentum of the atom $i$, and $\phi(r_{ij})$ is the interaction energy of atoms $i$ and $j$ separated by a distance $r_{ij}$. The partition function reads

$$\exp(-\beta F) \propto \int \exp\left(-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m}\right) \prod_{i=1}^{N} \mathrm{d}\mathbf{p}_i \underbrace{\int \exp\left(-\beta \sum_{i<j} \phi(r_{ij})\right) \prod_{i=1}^{N} \mathrm{d}\mathbf{r}_i}_{Z(T,V)} \,.$$

The integrals over the linear momenta are independent of volume and hence do not contribute to pressure. The remaining part of the partition function, which does depend on the positions of the atoms (and thus on volume) and is referred to as the configuration integral, is denoted by $Z(T, V)$

$$Z(T,V) = \int_V \exp\left(-\beta\sum_{j=2}^{N}\phi(r_{1j})\right)\mathrm{d}\mathbf{r}_1 \int_V \exp\left(-\beta\sum_{j=3}^{N}\phi(r_{2j})\right)\mathrm{d}\mathbf{r}_2 \times \\ \cdots \times \int_V \exp\left(-\beta\phi(r_{N-1\,N})\right)\mathrm{d}\mathbf{r}_{N-1}\int_V \mathrm{d}\mathbf{r}_N\,.$$

Each of the factors in the integrand can be recast as $\exp\left(-\beta\phi(r_{ij})\right) = 1 - \left[1-\exp\left(-\beta\phi(r_{ij})\right)\right]$. This form is convenient because the pair potential $\phi(r)$ decreases rapidly with distance, and thus the expression in the square brackets which depends on the pair potential is nonzero only if the distance between atoms $i$ and $j$ is small enough. When integrating, for example, over the position of the first atom ($\mathbf{r}_1$), the expression in square brackets differs from 0 only in the vicinity of each of the remaining $N-1$ atoms. Since all atoms are identical, the contributions of each of these regions to the part of the configuration integral in question denoted by $Z_1(T, V)$ are identical too (Fig. 9.10). At intermediate densities, the contributions of clusters containing more than two atoms can be neglected; in this case, the integral over $\mathbf{r}_1$ gives

$$\begin{aligned} Z_1(T,V) &= \int_V \left\{1-\left[1-\exp\left(-\beta\sum_{j=2}^{N}\phi(r_{1j})\right)\right]\right\}\mathrm{d}\mathbf{r}_1 \\ &= V - 2B_2(N-1)\,, \end{aligned}$$

where

$$B_2 = \frac{1}{2}\int_0^\infty \left[1-\exp\left(-\beta\phi(r)\right)\right]4\pi r^2\,\mathrm{d}r$$

is the second virial coefficient. Due to the rapid decrease of interaction with distance, the upper bound of the integral can be replaced by infinity. In a similar manner, we integrate over the remaining coordinates $\mathbf{r}_i$ to find that $Z_i(T, V) = V - 2B_2(N-i)$ so that in the configuration integral, the interaction between each pair of atoms appears only once as it should. Thus

$$Z(T,V) = \prod_{i=1}^{N} Z_i(T,V) = V^N \prod_{i=1}^{N}\left[1-\frac{2B_2(N-i)}{V}\right].$$

Upon taking the logarithm of the configuration integral one obtains

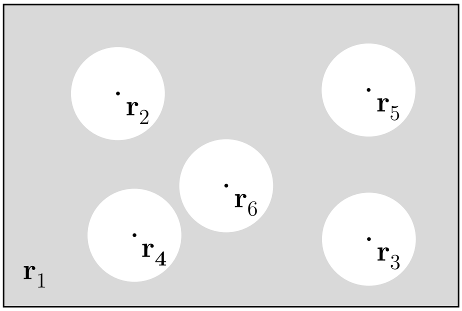

**Fig. 9.10** Virial equation of state: When integrating over the position of the first atom denoted by $\mathbf{r}_1$, all other atoms are fixed in space (plotted here is the $N = 6$ case). The integrand $1 - \exp\left[-\beta\phi(r_{1j})\right]$ is finite only within the white regions where the first atom is close to any of the other atoms whereas in the gray region it vanishes. At small enough densities, the white regions do not overlap and only two-atom clusters need to be considered. After the integral over $\mathbf{r}_1$ is evaluated, the circle belonging to the second atom is removed and we integrate over $\mathbf{r}_2$, etc. until the integrals over the positions of all atoms are carried out

$$\begin{aligned}\ln Z(T, V) &= N \ln V + \sum_{i=1}^{N-1} \ln\left(1 - \frac{2B_2(N-i)}{V}\right)\\ &\approx N \ln V - \sum_{i=1}^{N-1} \frac{2B_2(N-i)}{V}\\ &= N \ln V - \frac{B_2 N(N-1)}{V},\end{aligned}$$

where we assumed that $2B_2(N-i)/V \ll 1$ and recognized the arithmetic series. Since the number of atoms is large, we can replace $N(N-1)$ by $N^2$ to arrive at the virial equation of state

$$p = \frac{1}{\beta}\left(\frac{\partial \ln Z(T, V)}{\partial V}\right)_\beta \approx \frac{N k_B T}{V}\left(1 + \frac{N B_2}{V}\right).$$

The relative correction to the ideal gas equation of state $N B_2/V$ is proportional to the density, and is small if the density is small too because the magnitude of the second virial coefficient is determined by the range of the pair potential which is usually much less than the average distance between the atoms $(V/N)^{1/3}$.

A more general virial expansion of the equation of state reads

$$p = \frac{N k_B T}{V}\left[1 + \sum_{j=2}^{\infty} B_j(T)\left(\frac{N}{V}\right)^{j-1}\right].$$

The second virial coefficient reflects the interaction between pairs of atoms, whereas the higher terms correspond to triplets, quadruplets, etc. and cannot be evaluated analytically except in a few special cases. Alternatively, dense fluids and many other strongly correlated systems can be studied using computer simulations (Appendix B).

**Problem 9.14.**

*Derive the equation of state for a nonideal gas consisting of hard spheres of diameter* $\sigma$ *with an attractive interaction*

$$\phi(r) = \begin{cases} \infty, & r < \sigma \\ -\phi_0(\sigma/r)^s, & r \geq \sigma \end{cases},$$

*given that* $s > 3$ *and assuming that the attractive part of the potential is shallow so that* $\beta\phi_0 \ll 1$*! What is the internal energy of such a gas?*

For the given potential (plotted in Fig. 9.11) and $\beta\phi_0 \ll 1$ we have

$$1 - \exp\Big(-\beta\phi(r)\Big) \approx \begin{cases} 1, & r < \sigma \\ -\beta\phi_0(\sigma/r)^s, & r \geq \sigma \end{cases}.$$

The second virial coefficient is equal to

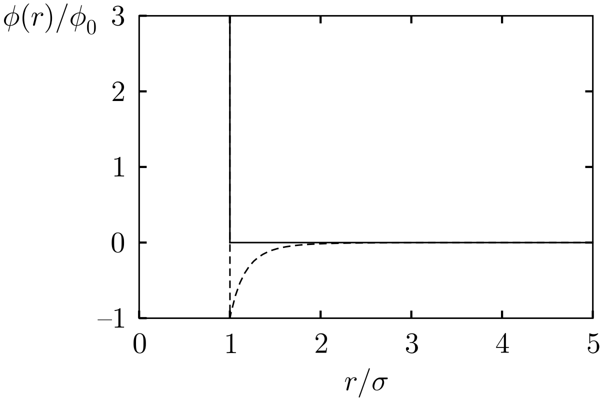

**Fig. 9.11** Interatomic potential in a nonideal gas: Hard-sphere repulsion (solid line) and hard-sphere repulsion combined with the van der Waals attraction ($s = 6$, dashed line)

$$B_2 = \frac{1}{2}\left[\int_0^\sigma 4\pi r^2\,\mathrm{d}r - \int_\sigma^\infty \beta\phi_0\left(\frac{\sigma}{r}\right)^s 4\pi r^2\,\mathrm{d}r\right] = 4V_0 - \beta\alpha\,.$$

The second integral converges only if $s > 3$; in the last step, we introduced $V_0 = \pi\sigma^3/6$ and $\alpha = 12V_0\phi_0/(s-3)$. For $\phi_0 \neq 0$, $B_2$ depends on temperature. The virial equation of state now reads

$$pV = Nk_BT\left[1 + \frac{N}{V}\left(4V_0 - \beta\alpha\right)\right],$$

and can be recast as

$$\left(p+\frac{N^2}{V^2}\alpha\right)(V-4NV_0)=Nk_BT\ .$$

It is instructive to compare this result with the van der Waals equation of state $(p+a/V^2)(V-b)=Nk_BT$: We notice that the coefficient $a=N^2\alpha$ originates from attractive interparticle forces, whereas the coefficient $b=4NV_0$ is the signature of hard-core repulsion.

The internal energy of a nonideal gas consists of a kinetic term which is the same as in the ideal gas and of an interaction term

$$U_i=-\left(\frac{\partial\ln Z(T,V)}{\partial\beta}\right)_V=\frac{N^2}{V}\frac{\mathrm{d}B_2}{\mathrm{d}\beta}=-\frac{N^2\alpha}{V}\ ;$$

the configuration integral $Z(T,V)$ is defined in Problem 9.13. The internal energy of a monatomic nonideal gas is given by

$$U(T,V)=\frac{3Nk_BT}{2}-\frac{N^2\alpha}{V}$$

and does not depend only on temperature like in an ideal gas but also on volume. In case of an attractive long-range interaction one has $\alpha>0$ and at a given $T$, $U$ is smaller than in an ideal gas, whereas otherwise $\alpha<0$ and $U$ is larger than in an ideal gas.

**Problem 9.15.**
*A monatomic gas, initially at a pressure of* 5 bar *and a temperature of* 27 °C, *flows through a thermally insulated valve into a chamber where the pressure is* 1 bar. *Calculate the change of temperature in this process! The interaction between the atoms is given by*

$$\phi(r)=\begin{cases}\infty, & r<\sigma\\ -\phi_0, & \sigma\le r<2\sigma\\ 0, & r\ge 2\sigma\end{cases}\ ,$$

*with* $\sigma=0.2$ nm *and* $\phi_0=10^{-3}$ eV. *For what values of the* $\phi_0$ *does the temperature of the gas increase?*

The gas undergoes the Joule–Kelvin process. The change of temperature can be calculated using the Joule–Kelvin coefficient $(\partial T/\partial p)_H=\left(\beta'T-1\right)/\rho c_p$, where $\beta'$ is the volumetric thermal expansion coefficient. For the given interatomic potential and $\beta\phi_0\ll 1$ we have

$$B_2=\frac{1}{2}\left(\int_0^\sigma 4\pi r^2\,\mathrm{d}r-\beta\phi_0\int_\sigma^{2\sigma}4\pi r^2\,\mathrm{d}r\right)=4V_0(1-7\beta\phi_0)\,,$$

where $V_0 = \pi\sigma^3/6$. Now we construct the virial equation of state, calculate the thermal expansion coefficient, and finally obtain

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{8V_0}{5k_B}\left(\frac{14\phi_0}{k_B T} - 1\right) = -2.23 \times 10^{-7}\ \mathrm{K/Pa}\,,$$

so that the temperature increases by 0.09 K; here we took into account that $c_p = 5R/2M$ and retained only the lowest-order terms.

The Joule–Kelvin coefficient changes sign at $14\phi_0 - k_B T = 0$; hence the temperature of the gas is increased for $\phi_0 < k_B T/14 = 1.85 \times 10^{-3}$ eV. A sudden drop of pressure leads to an increase of temperature only if the attractive tail of the interatomic potential is shallow enough for the repulsive forces to prevail in the system.

**Problem 9.16.**

*A thermally insulated evacuated vessel contains an ampoule of a volume of* $0.1\ \mathrm{dm}^3$ *filled by* $10^{-5}$ kmol *of gas characterized by intermolecular interaction considered in Problem* 9.15. *The initial temperature of the gas is* 27 °C. *What should be the volume of the container if the temperature of the gas is to decrease by* 0.02 °C *after the ampoule breaks?*

Since the container is both evacuated and thermally insulated, the internal energy of the gas is conserved after the ampoule is broken; this is an instance of the so-called Hirn experiment. As the gas involved is nonideal, its internal energy depends on volume and is equal to (see Problem 9.14)

$$U(T,V) = \frac{3N}{2\beta} + \frac{N^2}{V}\frac{\mathrm{d}B_2}{\mathrm{d}\beta} = \frac{3Nk_B T}{2} - \frac{28N^2V_0\phi_0}{V}\,.$$

Here we inserted $B_2$ calculated in Problem 9.15. Finally $U(V,T) = U(V',T')$ (here $V'$ is the volume of the ampoule, $T'$ is the initial temperature of the gas, $V$ is the volume of the container, and $T$ is the final temperature) gives

$$V = \left[\frac{1}{V'} - \frac{3k_B(T'-T)}{56NV_0\phi_0}\right]^{-1} = 0.158\ \mathrm{dm}^3\,.$$

**Problem 9.17.**

*The pair interaction between the atoms in a nonideal gas is described by a hard-sphere/square-well potential*

$$\phi(r) = \begin{cases} \infty, & r \le \sigma \\ -\phi_0, & \sigma < r \le 2\sigma \\ 0, & r > 2\sigma \end{cases}\,,$$

*where* $\sigma = 0.1$ *nm and* $\phi_0 = 5$ *meV. For not too dense a gas, derive the van der Waals form of the equation of state and express its parameters in terms of* $\phi_0$ *and* $\sigma$*, assuming that* $\phi_0 \ll k_B T$*! Estimate the critical parameters of the gas (pressure, temperature, and kilomolar volume)!*

We first calculate the second virial coefficient. By taking into account that $\phi_0 \ll k_B T$ one has

$$B_2 = \frac{2\pi\sigma^3}{3}\left(1 - 7\beta\phi_0\right).$$

Given that the density of the gas $N/V$ is not too high, i.e., $N\sigma^3/V \ll 1$, the virial equation of state can be rearranged into

$$\left(p + \frac{14\pi}{3}\frac{N^2\phi_0\sigma^3}{V^2}\right)\left(1 - \frac{2\pi}{3}\frac{N\sigma^3}{V}\right) = \frac{Nk_BT}{V}.$$

Now we express $V$ in terms of kilomolar volume $V_M = VN_A/N$ and we compare the obtained equation of state with the van der Waals form to find that the two parameters describing the nonideality of the gas read

$$a = \frac{14\pi}{3}N_A^2\phi_0\sigma^3 \qquad \text{and} \qquad b = \frac{2\pi}{3}\sigma^3 N_A\,.$$

By using the results of Problem 1.1 and by recalling that $R = k_B N_A$, we find that the critical pressure, temperature, and kilomolar volume are $p_c = 7\phi_0/18\pi\sigma^3 = 990\,\text{bar}$, $T_c = 56\phi_0/27k_B = 120$ K, and $V_{Mc} = 2\pi\sigma^3 N_A = 3.8\ \text{dm}^3/\text{kmol}$, respectively.

**Problem 9.18.**

*Explore the temperature dependence of heat capacity in a rarefied gas of particles characterized by the square-shoulder repulsive pair interaction*

$$\phi(r) = \begin{cases} \infty, & r < \sigma_1 \\ \phi_0, & \sigma_1 \le r < \sigma_2 \\ 0, & r \ge \sigma_2 \end{cases},$$

*where* $\sigma_2 > \sigma_1$ *and* $\phi_0 > 0$! *At what temperature does it reach a maximum?*

Since the gas is rarefied, the deviation of the heat capacity from the classical monatomic gas value can be described by the virial expansion (see Problem 9.13). The partition function reads

$$\exp(-\beta F) \propto \left(\frac{2\pi m}{\beta}\right)^{3N/2} V^N \left(1 - \frac{N^2 B_2}{V}\right),$$

where

$$B_2 = \frac{2\pi}{3}\left\{\sigma_1^3 + \left[1 - \exp(-\beta\phi_0)\right]\left(\sigma_2^3 - \sigma_1^3\right)\right\}.$$

The internal energy of the gas is given by

$$U = \left(\frac{\partial \beta F}{\partial \beta}\right)_V = N\left[\frac{3k_BT}{2} + \frac{2\pi N}{3V}\left(\sigma_2^3 - \sigma_1^3\right)\phi_0 \exp\left(-\frac{\phi_0}{k_BT}\right)\right],$$

so that

$$C_V = Nk_B\left[\frac{3}{2} + \frac{2\pi N}{3V}\left(\sigma_2^3 - \sigma_1^3\right)\left(\frac{\phi_0}{k_BT}\right)^2 \exp\left(-\frac{\phi_0}{k_BT}\right)\right].$$

The second term in the brackets represents the correction of the classical ideal gas value: It is proportional to the density and drops to zero at both very low and at very high temperature and exhibits a maximum at $T = \phi_0/2k_B$ in between (Fig. 9.12). The limits are easily understandable given that at low and high temperature the particles behave as hard spheres of diameter $\sigma_2$ and $\sigma_1$, respectively. As the heat capacity is unaffected by the proper volume of the particles, it is the same at both low and high temperature.

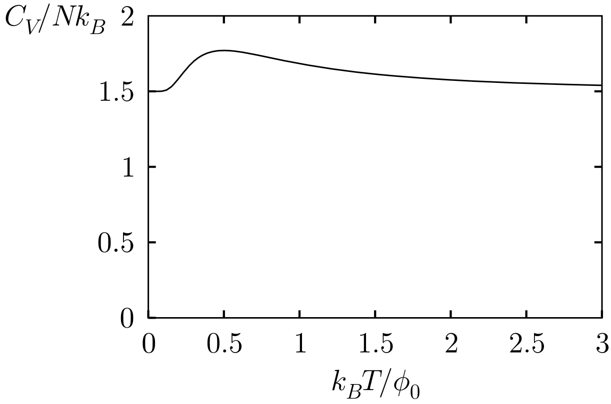

**Fig. 9.12** Heat capacity of a rarefied gas consisting of hard particles with an additional shoulder-like repulsive interaction features a maximum in between the low- and high-temperature limits where $C_V$ is equal to $3Nk_B/2$. To emphasize the maximum, $C_V$ is plotted at a relatively high density where $(2\pi N/3V)\left(\sigma_2^3 - \sigma_1^3\right) = 0.5$, where a more complete virial expansion is needed instead of the lowest-order approximation used here

**Problem 9.19.**

*Derive the equation of state for a one-dimensional gas consisting of particles interacting only with nearest neighbors! Consider a bare hard-sphere potential as well as a hard-sphere potential combined with a square-well attraction of finite depth and width!*

This model is known as the Tonks gas. In one dimension, the particles cannot jump past each other so that $x_1 < x_2 < \ldots < x_N$, where $x_i$ is the position of the $i$th particle and the particles are numbered consecutively from 1 to $N$. For simplicity, we use periodic boundary conditions so that the $N$th particle with $x_N = L$ reappears as the left neighbor of the first particle and formally $x_0 = 0$; here $L$ is the length (i.e., one-dimensional volume).

At constant $L$, the partition function is given by

$$\exp\bigl(-\beta F(T, L)\bigr) \propto \int \exp\bigl(-\beta\phi(x_1)\bigr)\exp\bigl(-\beta\phi(x_2 - x_1)\bigr) \times \cdots$$
$$\cdots \times \exp\bigl(-\beta\phi(L - x_{N-1})\bigr)\, \mathrm{d}x_1\mathrm{d}x_2 \cdots \mathrm{d}x_{N-1},$$

where the integrals are over all $x_j$ with $1 \leq j \leq N-1$ so that $0 < x_1 < x_2 < \cdots < L$. The partition function is to be evaluated only for configurations of particles arranged in sequential order so that $x_1 < x_2 < \cdots < x_N$, which is nontrivial. These technical difficulties can be bypassed by resorting to the Legendre transform to switch from the isochoric to the isobaric ensemble where pressure rather than volume is kept constant. The isobaric partition function reads

$$\begin{aligned}\exp\bigl(-\beta G(T,p)\bigr) \propto \int_0^\infty &\exp\bigl(-\beta\,[F(T,L)+pL]\bigr)\,\mathrm{d}L\\ = \int &\exp\bigl(-\beta\phi(y_1)\bigr)\exp\bigl(-\beta\phi(y_2)\bigr)\cdots\exp\bigl(-\beta\phi(y_N)\bigr)\\ &\times\exp\left(-\beta p\sum_{j=1}^{N} y_j\right)\mathrm{d}y_1\mathrm{d}y_2\cdots\mathrm{d}y_N\,,\end{aligned}$$

where

$$\begin{aligned}y_1 &= x_1\,,\\ y_{1<j<N} &= x_j - x_{j-1}\,,\\ y_N &= L - x_{N-1}\end{aligned}$$

are the relative particle coordinates with $0 < y_j < \infty$; we took into account that $L = \sum_{j=1}^{N} y_j$. Now we notice that the integrand actually consists of identical factors, yielding

$$\exp(-\beta G) \propto \left[\int_0^\infty \exp\bigl(-\beta\,[\phi(y)+py]\bigr)\,\mathrm{d}y\right]^N.$$

The equation of state can now be derived from the total differential $\mathrm{d}G = -S\,\mathrm{d}T + L\,\mathrm{d}p$ whereby $L = (\partial G/\partial p)_T$. We first calculate $L(p)$ for the hard-sphere interaction with the sphere diameter equal to $\sigma_1$. We obtain $\exp(-\beta G) \propto \left[\int_{\sigma_1}^\infty \exp(-\beta p y)\,\mathrm{d}y\right]^N = \left[\exp(-\beta p\sigma_1)/\beta p\right]^N$, which gives $G = Np\sigma_1 + N\ln(\beta p)/\beta$ and

$$\ell = \frac{L}{N} = \sigma_1 + \frac{k_B T}{p}$$

or $p = k_B T/(\ell - \sigma_1)$, which is reminiscent of the van der Waals equation of state for hard particles (see, e.g., Problem 9.17 for $\phi_0 = 0$). There is, however, an important difference: The van der Waals equation for a three-dimensional gas is derived using the (truncated) virial expansion and is thus valid only at low densities, whereas the above result is exact and holds at an arbitrary density.

We now consider a pair potential that includes a hard-sphere repulsion of range $\sigma_1$ and an attractive square-well tail of depth $-\phi_0 < 0$ and range $\sigma_2$. Then we have

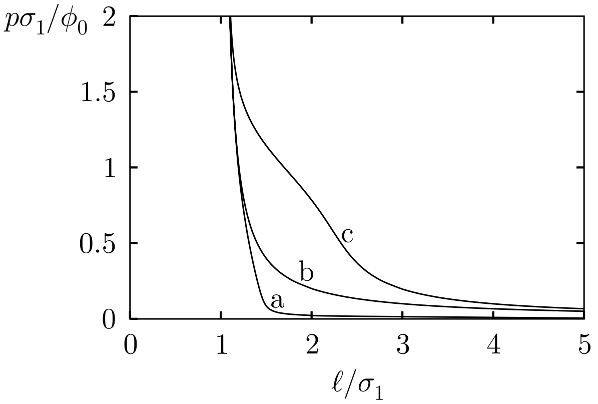

**Fig. 9.13** Isotherms of a one-dimensional gas consisting of hard-sphere/square-well particles of hard-core and well diameters $\sigma_1$ and $\sigma_2 = 2\sigma_1$, respectively, and well depth $-\phi_0$; the reduced temperature is $k_BT/\phi_0 = 0.2$ (a). Also plotted are the isotherms of a gas of hard-sphere particles of diameter $\sigma_1$ where $p = k_BT/(\ell - \sigma_1)$ (b), and of a gas of hard-sphere/square-shoulder particles of shoulder height $\phi_0$ and diameter $\sigma_2 = 2\sigma_1$ (c). In all three cases, the pressure is a monotonic function of $\ell$. In this respect, the isotherms are qualitatively the same at all temperatures, and thus there is no liquid-to-gas phase transition

$$\ell = \frac{\sigma_1 - \sigma_2 \exp\bigl(-p(\sigma_2 - \sigma_1)/k_BT\bigr)\left[1 - \exp(-\phi_0/k_BT)\right]}{1 - \exp\bigl(-p(\sigma_2 - \sigma_1)/k_BT\bigr)\left[1 - \exp(-\phi_0/k_BT)\right]} + \frac{k_BT}{p}\,.$$

In this case, the pressure cannot be expressed explicitly as a function of volume or density. This is actually not a problem as the equation of state can still be analyzed by plotting $\ell(p)$ instead. Figure 9.13 shows that the pressure is a monotonically decreasing function of $\ell$ at all temperatures. This means that in this one-dimensional model, there is no liquid–gas phase transition despite the attractive part of the pair potential. It turns out that no one-dimensional ensemble where particles interact only with a finite number of nearest neighbors features such a phase transition. This finding is known as the van Hove theorem.

**Problem 9.20.**

*Derive the relation between the radial distribution function and the interatomic potential! Calculate the radial distribution function for a gas consisting of particles with pair potential considered in Problem 9.14!*

The probability density $\rho(E)$ is a function of coordinates $\mathbf{r}_i$ and momenta $\mathbf{p}_i$ of the $N$ atoms in the ensemble. The probability density for finding the first atom at $\mathbf{r}_1$, the second atom at $\mathbf{r}_2$, …, is obtained by integrating $\rho(E)$ over the subspace spanned by the momenta

$$w_N(\mathbf{r}_1, \ldots \mathbf{r}_N) = \int \rho(\mathbf{r}_1, \ldots \mathbf{r}_N, \mathbf{p}_1, \ldots \mathbf{p}_N)\,\mathrm{d}\mathbf{p}_1 \cdots \mathrm{d}\mathbf{p}_N\,,$$

thereby projecting the probability density $\rho(\mathbf{r}_1, \ldots \mathbf{r}_N, \mathbf{p}_1, \ldots \mathbf{p}_N)$ onto the subspace of spatial coordinates. By further integrating over the positions of atoms $3, 4, \ldots N$, we define the two-particle distribution function:

$$w_2(\mathbf{r}_1, \mathbf{r}_2) = \int w_N(\mathbf{r}_1, \ldots \mathbf{r}_N)\, \mathrm{d}\mathbf{r}_3 \cdots \mathrm{d}\mathbf{r}_N\,,$$

which gives the probability density for finding atoms 1 and 2 at $\mathbf{r}_1$ and $\mathbf{r}_2$, respectively. We insert the normalized $w_N(\mathbf{r}_1, \ldots \mathbf{r}_N) \propto \exp\left(-\beta \sum_{i<j} \phi(r_{ij})\right)$ and assume that the density is low so that we can integrate it like in Problem 9.13 where we calculated the configuration integral $Z(T, V)$ but we omit the integrals over $\mathbf{r}_1$ and $\mathbf{r}_2$. Thus we find that

$$\begin{aligned} w_2(\mathbf{r}_1, \mathbf{r}_2) &= \frac{\left\{\prod_{i=3}^{N} [V - 2B_2(i-1)]\right\} \exp\left(-\beta\phi(r_{12})\right)}{\prod_{i=1}^{N} [V - 2B_2(i-1)]} \\ &= \frac{\exp\left(-\beta\phi(r_{12})\right)}{V(V - 2B_2)}\,. \end{aligned}$$

At low densities one has $V \gg 2B_2$ and hence

$$w_2(\mathbf{r}_1, \mathbf{r}_2) \approx \frac{1}{V^2} \exp\left(-\beta\phi(r_{12})\right) = \frac{1}{V^2} g(r_{12})\,,$$

where $g(r) = \exp\left(-\beta\phi(r)\right)$ is the radial distribution function. (No generality is lost by selecting atoms 1 and 2 out of $N$ identical atoms.)

In an ideal gas where $\phi(r_{12}) = 0$ the atoms are mutually independent, $w_2(\mathbf{r}_1, \mathbf{r}_2) = w_1(\mathbf{r}_1) w_1(\mathbf{r}_2)$. Here $w_1(\mathbf{r})$ is the single-particle distribution function; in a uniform gas $w_1(\mathbf{r}) = V^{-1}$.

It is often convenient to consider the local number density $n(\mathbf{r}) = N w_1(\mathbf{r})$ and describe pair correlations by introducing the two-particle number density

$$n(\mathbf{r}_1, \mathbf{r}_2) = N^2 w_2(\mathbf{r}_1, \mathbf{r}_2) = n^2 g(r_{12})\,,$$

where $n = N/V$ stands for the number density of a uniform gas. Thus we see that $g(r_{12})$ corresponds to the particle density at a distance $r_{12}$ from the reference particle divided by the average density.

In a gas consisting of attractive hard spheres from Problem 9.14 one has

$$g(r) \approx \begin{cases} 0, & r < \sigma \\ \exp\left(\beta\phi_0(\sigma/r)^s\right), & r \geq \sigma \end{cases}.$$

The probability that the distance between two particles is smaller than the sphere diameter $\sigma$ is equal to 0. On the other hand, the probability of finding the two spheres at a large separation is a constant because the pair potential vanishes as $r \to \infty$; thus $g(r \to \infty) \to 1$. At intermediate separations one has $g(r) \gtrsim 1$ because the probability of finding two spheres at a distance $r \gtrsim \sigma$ is somewhat higher than for $r \to \infty$ due to the attractive tail of the pair potential.

**Problem 9.21.**
*Assume that the radial distribution function for gaseous helium be given by*

$$g(r) = \begin{cases} 0, & r < \sigma \\ 1, & r \geq \sigma \end{cases},$$

*where* $\sigma = 0.2$ nm. *Identify the corresponding interatomic potential, assuming that the density is not too high! At the level of linear corrections to the ideal gas equation of state, calculate the bulk thermal expansion coefficient of the gas at a density of* $10\ \mathrm{kg/m^3}$ *and a temperature of* $20\,^\circ\mathrm{C}$ *as well as the difference of heat capacities* $c_p - c_V$*! Compare the results with those for ideal gas! The kilomolar mass of helium is* 4 kg/kmol.

The relation $\phi(r) = -k_BT \ln\big(g(r)\big)$ (see Problem 9.20) suggests that $\phi(r)$ is the hard-sphere potential, the sphere diameter being $\sigma$. The corresponding equation of state is a special case of the van der Waals equation without the attractive tail (Problem 9.14; $\phi_0$ and hence $\alpha$ both vanish). The bulk thermal expansion coefficient is then

$$\beta' = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{T}\left(1 - \frac{4NV_0}{V}\right) = 3.33 \times 10^{-3}\ \mathrm{K}^{-1}\,.$$

The relative deviation from the ideal gas result is given by $4NV_0/V = 4V_0N_A\rho/M = 2.5\,\%$; here we used $V_0 = \pi\sigma^3/6$.

The difference of heat capacities is equal to

$$c_p - c_V = \frac{\beta'}{\rho}\left[p + \left(\frac{\partial U}{\partial V}\right)_T\right],$$

where $U$ stands for the internal energy. For a hard-sphere potential, $U$ contains only the kinetic term, $3Nk_BT/2$, and is hence independent of volume. Therefore at the lowest order we are left with

$$c_p - c_V = \frac{\beta' p}{\rho} \approx \frac{N_Ak_B}{M} = \frac{R}{M} = 2080\ \mathrm{J/kgK}$$

just like in an ideal gas.

**Problem 9.22.**
*The pair interaction between dendrimer molecules is given by a soft potential*

$$\phi(r) = \phi_0 \exp\left(-\frac{r^2}{\sigma^2}\right),$$

*where* $\phi_0 = 5 \times 10^{-4}$ eV *and* $\sigma = 5$ nm. *Calculate the relative deviation of its isothermal compressibility in the gas at* 300 K *and a number density of* $10^{24}$

*molecules per* m$^3$ *from that in an ideal gas! By how much does the density at a distance $\sigma$ from the center of a reference molecule differ from the average density?*

We first calculate the second virial coefficient by noting that $\beta\phi_0 \ll 1$ and expanding the exponential to first order. This gives

$$B_2 \approx \frac{1}{2}\int_0^\infty \beta\phi(r)4\pi r^2 \mathrm{d}r = \frac{\pi^{3/2}\beta\phi_0\sigma^3}{2}.$$

The virial equation of state thus reads

$$p = \frac{N}{V}k_BT + \left(\frac{N}{V}\right)^2 \frac{\pi^{3/2}\phi_0\sigma^3}{2}$$

and is differentiated at a constant temperature to give the isothermal compressibility

$$\chi_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \frac{V}{Nk_BT}\left(1 - \frac{N}{V}\frac{\pi^{3/2}\phi_0\sigma^3}{k_BT}\right).$$

The second term in the brackets corresponds to the relative deviation of $\chi_T$ from its ideal gas counterpart $V/Nk_BT$ and is small, amounting to 1.3%; in the above analysis, we already took this into account.

The ratio of the density at a certain distance $r$ from the reference molecule and the average density is given by the radial distribution function $g(r)$. In a rarefied gas one has $g(r) = \exp\left(-\beta\phi(r)\right)$ (Problem 9.20) and the corresponding difference of the number density of molecules reads

$$\Delta n = \frac{N}{V}\left[g(\sigma) - g(\infty)\right] \approx -\frac{N}{V}\beta\phi_0 \exp(-1) = -7.1 \times 10^{21}\ \mathrm{m}^{-3}.$$

Due to the soft repulsive potential, the density in the vicinity of each particle is decreased relative to that at a large distance.

## Problem 9.23.

*Derive the radial distribution function of a one-dimensional hard-sphere gas (Tonks gas)!*

In a homogeneous system, the particle density $n(\mathbf{r}) = \left\langle\sum_i \delta(\mathbf{r} - \mathbf{r}_i)\right\rangle$ (where the $i$ runs over all particles and the brackets denote thermodynamic averaging) is dependent of position and equal to $n = N/L$. (Here we use the same notation as in Problem 9.19.) The two-particle number density defined by

$$n(\mathbf{r}, \mathbf{r}') = \left\langle \sum_i \sum_{j\neq i} \delta(\mathbf{r} - \mathbf{r}_i)\delta(\mathbf{r}' - \mathbf{r}_j)\right\rangle,$$

can also be written as a product of the probability of finding a particle at $\mathbf{r}$ and of the conditional probability of finding another particle at $\mathbf{r}'$, provided that the first one is at **r**. In terms of number densities,

$$n(\mathbf{r},\mathbf{r}') = n(\mathbf{r}')\,n(\mathbf{r}|\mathbf{r}')\,.$$

In a homogeneous system the two-particle density depends only on the interparticle distance and like in Problem 9.20 we have

$$n(\mathbf{r},\mathbf{r}') = n^2 g(\mathbf{r}-\mathbf{r}')\,,$$

where $g(\mathbf{r}-\mathbf{r}')$ is the radial distribution function. By putting the second particle in the origin ($\mathbf{r}'=0$), we see that $g(\mathbf{r}) = n^{-1}n(\mathbf{r}|0)$.

In a one-dimensional system from Problem 9.19, the position of the left-most (0th) particle is fixed ($x_0 = 0$), whereas for the remaining particles $x_{j>0} > 0$. Now we introduce $g^+(x)$ by

$$ng^+(x) = n(x|0) = \left\langle \sum_{j>0} \delta(x-x_j) \right\rangle .$$

In the next step, we symmetrize the system by shifting its right half where $x$ is between $L/2$ and $L$ by $L$ to the left; this can be done because we use periodic boundary conditions. After we do so, we can extend the radial distribution function to all $x$ by introducing $g(x) = g^+(x) + g^+(-x)$.

We now calculate $g^+$. According to the above definition, it consists of terms corresponding to correlations between the 0th and the $j$th particle:

$$g^+(x) = \sum_{j=1}^{N-1} g^{(j)}(x)\,,$$

where $ng^{(j)}(x) = \langle \delta(x-x_j)\rangle$. The Laplace transform of $ng^{(j)}$ is

$$ng^{(j)}(\lambda) = \int_0^\infty \exp(-\lambda x)\langle\delta(x-x_j)\rangle\,\mathrm{d}x = \langle\exp(-\lambda x_j)\rangle\,.$$

Like in Problem 9.19 the statistical average is calculated by switching from the isochoric ($L = const.$) to the isobaric ensemble ($p = const.$). We introduce the relative coordinates of the particles $y_j = x_j - x_{j-1}$ so that $x_j = \sum_{i=1}^{j} y_i$. Then we have $ng^{(j)}(\lambda) = \big\langle \exp\big(-\lambda\sum_{i=1}^{j} y_i\big)\big\rangle$ and in case of a nearest-neighbor interaction $\phi = \phi(y_i)$, the average product of exponentials reduces to a product of averages of exponentials:

$$\begin{aligned} ng^{(j)}(\lambda) &= \prod_{i=1}^{j} \frac{\int_0^\infty \exp\big(-\beta\,[\phi(y_i)+py_i]\big)\exp(-\lambda y_i)\,\mathrm{d}y_i}{\int_0^\infty \exp\big(-\beta\,[\phi(y_i)+py_i]\big)\,\mathrm{d}y_i} \\ &= \langle\exp(-\lambda y)\rangle^j\,. \end{aligned}$$

We see that the Laplace transform of the correlation function between the 0th and $j$th particle $g^{(j)}(\lambda)$ is proportional to the $j$th power of the Laplace transform of the nearest-neighbor correlation function $ng^{(1)}(\lambda)$. This means that $g^{(j)}(x)$ is proportional to the convolution of $g^{(1)}(x)$:

$$g^{(j)}(x) = \underbrace{g^{(1)}(x) * g^{(1)}(x) * \cdots * g^{(1)}(x)}_{j}\, n^{j-1}\,.$$

We note that the same result can be derived without resorting to the Laplace transform by recalling that the probability distribution of a sum of two independent random variables—in this case the nearest-neighbor distances—is equal to a convolution of the single-variable probability distributions.

Using this apparatus, we readily obtain $g^{(1)}(x)$:

$$g^{(1)}(x) = \frac{1}{n}\frac{\exp\bigl(-\beta\,[\phi(x) + px]\bigr)}{\int_0^\infty \exp\bigl(-\beta\,[\phi(y) + py]\bigr)\,\mathrm{d}y}\,.$$

In our case, $\phi(x)$ is the hard-sphere interaction, i.e., $\phi(x < \sigma) \to \infty$ and $\phi(x > \sigma) = 0$, and the integral in the denominator equals $\exp(-\beta p\sigma)/\beta p$. We have

$$g^{(1)}(x) = \frac{1}{n}\frac{\beta p}{\exp(-\beta p\sigma)} \times \begin{cases} 0, & x < \sigma \\ \exp(-\beta px), & x \geq \sigma \end{cases}.$$

It is easy to see that as $p \to 0$, $g^{(1)}(x)$ approaches the Heaviside function because in this limit the equation of state reduces to $\beta p \approx n$ (Problem 9.19).

Now $g^{(2)}(x) = ng^{(1)}(x) * g^{(1)}(x)$ can be calculated directly using the formula $(u * v)(x) = \int_0^x u(z)v(x - z)\,\mathrm{d}z$. We obtain

$$g^{(2)}(x) = \frac{1}{n}\left[\frac{\beta p}{\exp(-\beta p\sigma)}\right]^2 \times \begin{cases} 0, & x < 2\sigma \\ (x - 2\sigma)\exp(-\beta px), & x \geq 2\sigma \end{cases}.$$

The higher order correlation functions $g^{(j)}$ are calculated analogously one after another.

Before plotting the obtained radial distribution function we recall that density, pressure, and temperature are related by the equation of state; for hard spheres it reads $n^{-1} = L/N = \sigma + 1/\beta p$ (Problem 9.19). The full $g^{+}(x)$, which at $x < 3\sigma$ consists of $g^{(1)}(x)$ and $g^{(2)}(x)$, is depicted in Fig. 9.14. At high pressures, the pair correlation function consists of a series of peaks separated approximately by $\sigma$. The height of the peaks decreases with increasing distance from the reference particle, whereas their width increases. In the correlation holes between the peaks the radial distribution function drops significantly. At low pressures, however, the structure of $g^{+}$ is less pronounced: The peaks are lower and the holes are shallower. As already mentioned, $g^{+}(x) \approx g^{(1)}(x)$ for $p \to 0$; as a result, the radial distribution function reduces to the Heaviside function, which agrees with the solution of Problem 9.20.

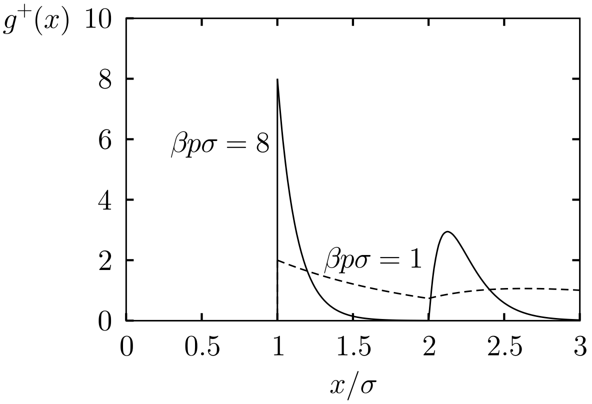

**Fig. 9.14** Radial distribution function of a one-dimensional hard-sphere ensemble: At high pressures, the peaks and the correlation holes are quite prominent ($\beta p\sigma = 8$; solid line) whereas at low pressures ($\beta p\sigma = 1$; dashed line), the radial distribution function is less structured and approaches the Heaviside function for $p \to 0$

**Problem 9.24.**

*Derive the equation of state for plasma using the Debye–Hückel approximation where one assumes that each ion is exposed to a mean field of counterions!*

Plasma is a gas consisting of cations and electrons. Since the electrostatic force between these particles is long-range, the equation of state cannot be constructed using a virial expansion. Namely, the second virial coefficient does not converge: For $r \to \infty$, $B_2 = (1/2)\int_0^\infty \left[1 - \exp\left(-\beta q_i q_j / 4\pi\epsilon_0 r\right)\right] 4\pi r^2\,\mathrm{d}r$ behaves approximately as $(\beta q_i q_j / 2\epsilon_0)\int^\infty r\,\mathrm{d}r$ and hence diverges; here $q_i$ and $q_j$ denote the charges of the particles. However, physically the structure of plasma is quite clear: Each of the cations is surrounded by an electron cloud, which screens the charge of the cation (Fig. 9.15). This is not taken into account by the virial formalism at the level of second virial coefficient, which includes only pair interactions.

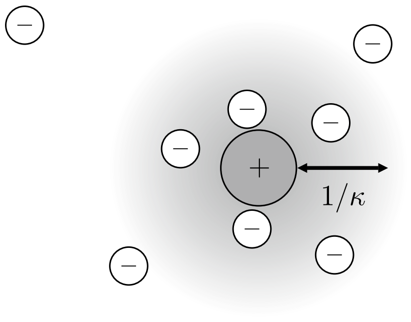

**Fig. 9.15** Screening in plasma: Each cation is surrounded by an electron cloud of a radius given by the screening length $1/\kappa$. (The sketch ignores the fact that the number of cations and electrons must be equal to ensure electroneutrality)

We, therefore, take a different route and describe screening using a continuum model, restricting the discussion to two-component plasma with the two ion species denoted by subscripts 1 and 2. The charges of two ion species are equal and opposite, i.e., $q_1 = +q$ and $q_2 = -q$, whereas their average number densities are the same ($N_1/V = N_2/V = n$) as the system as a whole must be neutral so that $N_1 q_1 + N_2 q_2 = (N_1 - N_2)\, q = 0$. We consider hot rarefied plasma where the total electrostatic energy estimated by $\left(q^2/4\pi\epsilon_0\right)\langle r^{-1}\rangle \sim q^2 n^{1/3}/4\pi\epsilon_0$ (where $n^{-1/3}$ represents an approximate average ion-to-ion distance) is small compared to the average kinetic energy equal to $3k_B T/2$. Thus in hot rarefied plasma

$$n \ll \left(\frac{6\pi k_B T\epsilon_0}{q^2}\right)^3 .$$

Now we analyze the electric field around an ion of species 1. The Gauss law $\nabla \cdot \mathbf{D} = \rho_e$, where $\mathbf{D} = -\epsilon_0 \nabla\phi_1$, can be recast as

$$\nabla^2\phi_1 = -\frac{1}{\epsilon_0}\left[q n_1(\mathbf{r}) - q n_2(\mathbf{r})\right],$$

where $\phi_1$ is the electric potential around the reference ion, whereas $n_1(\mathbf{r})$ and $n_2(\mathbf{r})$ are the position-dependent densities of the remaining ions of species 1 and 2, respectively. The local density of ions is determined by the Maxwell–Boltzmann distribution

$$n_i(\mathbf{r}) = n \exp\left(-\frac{q_i\phi_1(\mathbf{r})}{k_B T}\right),$$

which makes the Gauss law nonlinear. In the Debye–Hückel approximation applicable at high temperatures, the exponential can be expanded which yields $\rho_e \approx -2q^2 n\phi_1/k_B T$. Then one has

$$\nabla^2\phi_1 = \kappa^2\phi_1 ,$$

where $\kappa$ stands for $\sqrt{2q^2 n/k_B T\epsilon_0}$. Since $\phi_1$ is spherically symmetric and the radial part of $\nabla^2$ is equal to $\mathrm{d}^2/\mathrm{d}r^2 + (2/r)\,\mathrm{d}/\mathrm{d}r$, we find that $\phi_1(r) \propto \exp(-\kappa r)/r$. More precisely, as for $r \to 0$ the potential has to agree with that of a bare ion of species 1, we have

$$\phi_1(r) = \frac{q}{4\pi\epsilon_0 r}\exp(-\kappa r) .$$

In plasma physics, this result is known as the Debye–Hückel potential, whereas in nuclear physics, it is referred to as the Yukawa potential. We notice that $\kappa^{-1}$ corresponds to the screening length, i.e., the size of the cloud of counterions around the reference ion. In hot rarefied plasma $n^{-1/3} \ll \kappa^{-1}$, indicating that this cloud contains many particles so that the continuum description used here is justified.

The correction of the internal energy due to electrostatic interactions between the ions is equal to $\Delta U = (1/2)\left(N_1 q_1 \widetilde{\phi_1} + N_2 q_2 \widetilde{\phi_2}\right)$, where $N_1$ and $N_2$ are the numbers of particles for each species and $\widetilde{\phi}_i$ the electric potential felt by ion $i$. (With the factor of $1/2$ we avoid counting each pair interaction twice.) By taking into account electroneutrality and the fact that $q_2 = -q_1 = -q$, we obtain

$$\Delta U = qN\widetilde{\phi}_1 ;$$

here $N$ is the total number of ions of either species.

We must still determine $\widetilde{\phi}_1$. To this end, $\phi_1$ is expanded for small $r$:

$$\phi_1(r) \approx \frac{q}{4\pi\epsilon_0}\frac{1-\kappa r+\mathcal{O}(r^2)}{r} = \frac{q}{4\pi\epsilon_0 r} - \frac{q\kappa}{4\pi\epsilon_0} + \mathcal{O}(r) .$$

The first term represents the potential of a bare ion 1, whereas the second one is the potential of the cloud of counterions at the site of ion 1 which represents the desired $\widetilde{\phi}_1$. The terms dropped are equal to 0 in the limit of $r \to 0$. Finally we have

$$\Delta U = -\frac{aN^{3/2}}{(VT)^{1/2}} ,$$

where $a = q^3/\pi(2\epsilon_0)^{3/2}k_B^{1/2}$.

Now the equation of state can be obtained using purely thermodynamical considerations, following the approach of Problem 4.10. From the internal energy $U(T,V) = U_{\rm id}(T) - aN^{3/2}/(VT)^{1/2}$ [where $U_{\rm id}(T) = 3Nk_BT/2$ is the internal energy of the ideal gas] we find

$$T^2\left(\frac{\partial(p/T)}{\partial T}\right)_V = T\left(\frac{\partial p}{\partial T}\right)_V - p = \left(\frac{\partial U}{\partial V}\right)_T = \frac{aN^{3/2}}{2V^{3/2}T^{1/2}} .$$

By dividing by $T^2$ and integrating over $T$ we obtain

$$p = -\frac{aN^{3/2}}{3V^{3/2}T^{1/2}} + T\varphi(V) ,$$

where $\varphi(V)$ is a function of volume still to be determined. For $V \to \infty$, we must recover the ideal gas equation of state $p_{\rm id} = Nk_BT$ so that $\varphi(V) = Nk_B$. In summary,

$$p = p_{\rm id} - \frac{aN^{3/2}}{3V^{3/2}T^{1/2}} .$$

Due to the attractive forces between the oppositely charged ions, the pressure of plasma is lower than in an ideal gas; screening evidently weakens the repulsive interactions between like-charge ions.

# Chapter 10
# Entropy

**Problem 10.1.**
*Assume that the shape of a liquid crystal molecule can be modeled by a hard spherocylinder of diameter $\sigma$ and length $d$. An orientationally perfectly ordered sample is confined between two parallel plates. Find the equilibrium molecular orientation, provided that the interaction between the molecules and the plates is purely steric!*

The volume of the positional phase space of each molecule depends on its orientation. Figure 10.1 shows that the center of mass of a molecule cannot approach the plate by less than $[\sigma + (d - \sigma)\cos\theta]/2$, where $d$, $\sigma$, and $\theta$ denote the length, diameter, and tilt of the spherocylinder, respectively.

This distance represents the thickness of the depletion zone at the plate that is inaccessible to the center of mass of the molecule; the volume of these zones is referred to as the excluded volume. Hence the remaining available volume is

$$V_a = A\left[h - \sigma - (d - \sigma)\cos\theta\right],$$

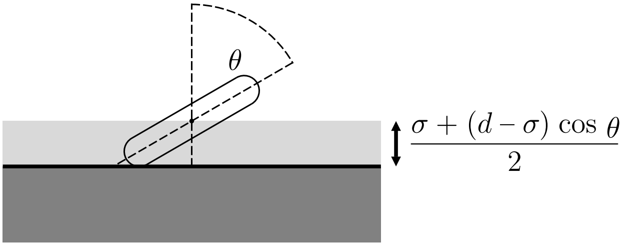

**Fig. 10.1** Spherocylinder at a plate: The smallest distance between the center of mass of the spherocylinder and the plate depends on tilt angle $\theta$; the corresponding depletion zone is shown in light gray

G. Skačej and P. Ziherl, *Solved Problems in Thermodynamics and Statistical Physics*, https://doi.org/10.1007/978-3-030-27661-4_10

where $A$ is the surface area of the plates and $h$ is the width of the gap between the plates. Since the probability density within the accessible part of phase space is constant, we have $\exp\bigl(-\beta F(\theta)\bigr) \propto \bigl[\int \exp\bigl(-\beta\phi(\mathbf{r})\bigr)\mathrm{d}\mathbf{r}\bigr]^N = V_a^N$, where the irrelevant degrees of freedom are omitted and we consider only the $\theta$-dependent part of the partition function, assuming that the molecules are independent; $N$ is the number of molecules. It is convenient to use $F(\pi/2)$ as the reference Helmholtz free energy and consider the difference

$$\begin{aligned} F(\theta) - F(\pi/2) &= -Nk_BT \ln \frac{h-\sigma-(d-\sigma)\cos\theta}{h-\sigma} \\ &\approx Nk_BT\frac{d-\sigma}{h}\cos\theta\,, \end{aligned}$$

where in the end we assumed that $h \gg d, \sigma$. The thus obtained "anchoring" term of the Helmholtz free energy of liquid-crystalline molecules is smallest for $\theta = \pi/2$ which corresponds to the planar alignment, and decreases approximately as $h^{-1}$ at large $h$.

We note that the origin of this free energy term is entirely entropic. This can be readily appreciated by calculating the internal energy of the ensemble given by $U = \mathrm{d}\beta F/\mathrm{d}\beta$. We find that apart from the kinetic term which is unimportant in the context of anchoring, $U$ is equal to 0. This is a consequence of the steric nature of the interaction between the model molecules and the plates. As the internal energy associated with anchoring vanishes, the corresponding Helmholtz free energy consists solely of the $-TS$ term. Such systems are referred to as "athermal" because their behavior is independent of temperature, which merely rescales the value of the Helmholtz free energy proportional to $T$.

**Problem 10.2.**
*Two parallel plates with a surface area of* $1\ \mathrm{mm}^2$ *are immersed in a suspension of small hard spheres* $100\ \mathrm{nm}$ *in diameter; the distance between the plates is* $75\ \mathrm{nm}$. *Calculate the force between the plates if the number density of the spheres is* $10^{18}/\mathrm{m}^3$ *and the temperature is* $20\,^\circ\mathrm{C}$*!*

If the plate-to-plate separation $h$ exceeds the diameter of the spheres $\sigma$, the excluded volume inaccessible to the spheres' centers of mass is equal to $2A\sigma$, where $A$ denotes the surface area of the plates (Fig. 10.2). The available volume is

$$V_a(h > \sigma) = V - 2A\sigma\,,$$

where $V$ denotes the total volume of the suspension. For plate-to-plate separations smaller than $\sigma$, the spheres cannot enter the gap between the plates and the excluded volume is equal to $A(\sigma + h)$ (Fig. 10.2). Consequently, the available volume is

$$V_a(h < \sigma) = V - A(\sigma + h)\,.$$

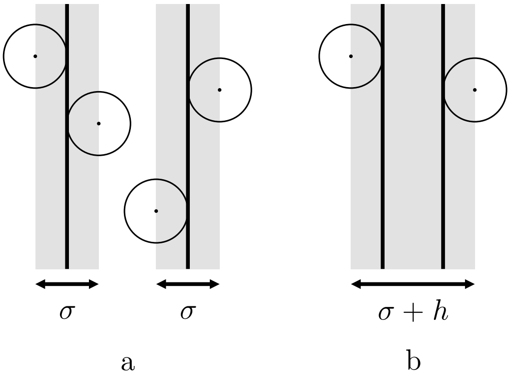

**Fig. 10.2** For plate-to-plate separations larger than the diameter of the spheres the volume of the depletion zones (shown in light gray) does not depend on separation (**a**), whereas otherwise (**b**) it does since the spheres cannot enter into the gap between the plates. This induces the so-called depletion force

The Helmholtz free energy is calculated like in Problem 10.1. A convenient choice of the reference Helmholtz free energy is the $h > \sigma$ value which is independent of the separation: In this case the interaction free energy reads

$$F(h) = \begin{cases} -Nk_BT \ln \dfrac{V - A(\sigma + h)}{V - 2A\sigma}, & h < \sigma \\ 0, & h > \sigma \end{cases},$$

where $N$ is the number of spheres. By taking into account that usually $V \gg 2A\sigma$, $A(\sigma + h)$ and performing a series expansion, we find that the final form of the interaction free energy reads

$$F(h) = \begin{cases} -nk_BTA(\sigma - h), & h < \sigma \\ 0, & h > \sigma \end{cases},$$

where $n = N/V$ denotes the number density of spheres. We conclude that for $h < d$ the force between the plates is attractive and independent of separation:

$$\mathcal{F} = -\left(\frac{\partial F}{\partial h}\right)_T = -nk_BTA\,.$$

For the given data, $\mathcal{F} = -4.04$ nN. For $h < \sigma$, this so-called depletion attraction results from the pressure of the gas of spheres acting on each plate from the outside but not from the inside as the spheres cannot enter the gap between the plates. On the other hand, for $h > \sigma$ the pressure is the same on both sides of the plates; therefore, no net attraction is observed.

**Problem 10.3.**
*Calculate the force between two flat membranes of surface area of* $1\ \mathrm{mm}^2$ *separated by* $0.1\ \mu\mathrm{m}$ *and immersed into a* $0.01\%$ *water solution of tobacco mosaic virus at* $20\,^\circ\mathrm{C}$*! The virus is a* $0.3\ \mu\mathrm{m}$*-long hard rod with an approximate kilomolar mass of* $3.1 \times 10^7$ kg/kmol.

The relevant part of the phase space depends on the position and the orientation of the rods; the latter is given by the polar angle $\theta$ (measured with respect to the membrane normal) and by the azimuthal angle $\phi$, which is unimportant in the present context. Note that the rods are characterized by head–tail symmetry and thus the polar angles $\theta$ and $\pi - \theta$ correspond to the same state; therefore, it suffices to consider only tilts between 0 and $\pi/2$. At a given $\theta$, the closest distance between the center of mass of the rod and the membrane is $(d/2)\cos\theta$, where $d$ is the rod length.

For membranes separated by $h > d$, the partition function reads

$$\begin{aligned}\exp\bigl(-\beta F(h > d)\bigr) &\propto \int_0^{\pi/2} \sin\theta\,\mathrm{d}\theta \int_{V_a(\theta)} \mathrm{d}\mathbf{r} \\ &= \int_0^{\pi/2} (V - 2Ad\cos\theta)\sin\theta\,\mathrm{d}\theta \\ &= V - Ad\,,\end{aligned}$$

where we took into account that the available volume at a fixed $\theta$ is given by $V_a(\theta) = V - 2Ad\cos\theta$; here $A$ stands for the surface area of the membranes. For $h < d$, there exist two regimes: When $\theta$ exceeds

$$\theta_{\min} = \arccos\left(\frac{h}{d}\right),$$

the rod can enter into the gap between the membranes and one has $V_a(\theta) = V - 2Ad\cos\theta$ as before, whereas in the opposite case the rod cannot fit between the membranes and $V_a(\theta) = V - A\,(d\cos\theta + h)$. We obtain

$$\begin{aligned}\exp\bigl(-\beta F(h < d)\bigr) &\propto \int_0^{\theta_{\min}} [V - A\,(d\cos\theta + h)]\sin\theta\,\mathrm{d}\theta \\ &\quad + \int_{\theta_{\min}}^{\pi/2} (V - 2Ad\cos\theta)\sin\theta\,\mathrm{d}\theta \\ &= V - Ad + \frac{Ad}{2}\left(1 - \frac{h}{d}\right)^2.\end{aligned}$$

Like in Problem 10.2, the Helmholtz free energy is calculated with respect to $F(h > d)$, yielding

$$F(h) = \begin{cases} -Nk_BT\ln\dfrac{V - Ad + Ad\,(1 - h/d)^2/2}{V - Ad}, & h < d \\ 0, & h > d \end{cases}.$$

Again we assume that $V \gg Ad$, $Ah$ which gives

$$F(h) = \begin{cases} -nk_BTAd\,(1-h/d)^2/2, & h < d \\ 0, & h > d \end{cases},$$

where $n = N/V$. The range of the thus obtained depletion attraction depicted in Fig. 10.3 is $h = d$ and the force reads

$$\mathcal{F} = -\left(\frac{\partial F}{\partial h}\right)_T = -nk_BTA\left(1 - \frac{h}{d}\right).$$

The numerical result: For the given kilomolar mass, the virus number density in a 0.01 % water solution is $1.94 \times 10^{18}/\mathrm{m}^3$ and the attractive force between two membranes with a surface area of 1 mm$^2$ is equal to −5.23 nN.

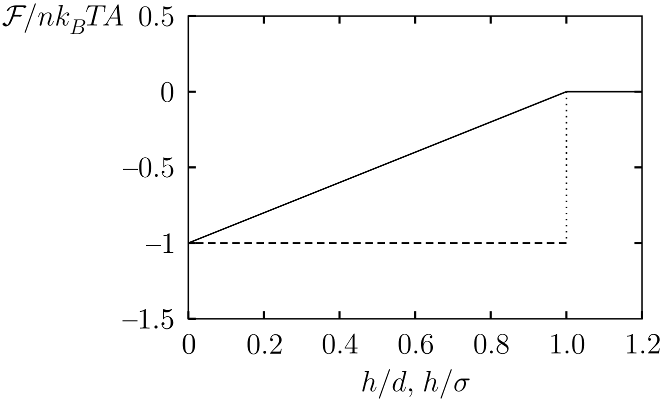

**Fig. 10.3** Depletion force between two parallel membranes separated by $h$ induced by hard rods of length $d$ (solid line) compared to that due to hard spheres of diameter $\sigma$ (dashed line; Problem 10.2). The range of the depletion force is equal to the size of the particles that induce the force

We conclude by suggesting a shortcut leading directly to the same result. The depletion interaction induced by the rods can also be obtained by treating the rods tilted at an angle $\theta$ as spheres of an effective diameter $d\cos\theta$. Now we take into account that only spheres satisfying the $d\cos\theta > h$ condition contribute to depletion and use the result of Problem 10.2 to find that

$$F(h < d) = -nk_BTA\int_0^{\theta_{\min}} (d\cos\theta - h)\sin\theta\,\mathrm{d}\theta\,.$$

**Problem 10.4.**
*Calculate the force between two identical hard spheres in a polystyrene solution at* 20 °C*! The radii of the spheres are* 1 $\mu$m *and their center-to-center distance* 2.1 $\mu$m*. A polystyrene molecule can be represented by a spherical aggregate of a radius of* 80 nm, *and one liter of the solution contains* $1.3 \times 10^{22}$ *such aggregates.*

The answer can be obtained by retracing the solution to Problem 10.2. As long as the distance between the centers of the spheres denoted by $h$ exceeds $2R+\sigma$ (here $R$ is the radius of the spheres and $\sigma$ is the diameter of a polystyrene molecule), the volume available to each polystyrene molecule in the solution is equal to

$$V_a\Big(h > 2R+\sigma\Big) = V - \frac{8\pi}{3}\left(R+\frac{\sigma}{2}\right)^3,$$

where $V$ stands for the total volume of the system. For $h$ smaller than $2R+\sigma$, however, the available volume increases due to the partial overlap of the excluded volumes of the spheres. Their intersection is represented by a lens-like body consisting of two identical spherical caps of thickness $\ell = R+\sigma/2-h/2$ and a total volume of $2\pi\ell^2\left[3\left(R+\sigma/2\right)-\ell\right]/3$. From here one has

$$\begin{aligned} V_a\big(h < 2R+\sigma\big) = V &- \frac{8\pi}{3}\left(R+\frac{\sigma}{2}\right)^3 \\ &+\frac{2\pi}{3}\left(R+\frac{\sigma}{2}-\frac{h}{2}\right)^2\left(2R+\sigma+\frac{h}{2}\right). \end{aligned}$$

We express the Helmholtz free energy relative to $F\big(h > 2R+\sigma\big)$ and we take into account that the total volume is much larger than the excluded volume. Thus we obtain

$$F(h) = \begin{cases} -\pi n k_B T\left(2R+\sigma-h\right)^2\left(2R+\sigma+h/2\right)/6, & h < 2R+\sigma \\ 0, & h > 2R+\sigma \end{cases}.$$

The attractive depletion force arises at sphere separations $h$ between $2R$ and $2R+\sigma$ and is equal to

$$\mathcal{F} = -\pi n k_B T\left(R+\frac{\sigma-h}{2}\right)\left(R+\frac{\sigma+h}{2}\right);$$

at the given input data $\mathcal{F} = -10.55$ pN.

### Problem 10.5.

*A pair of parallel plates is immersed into a dilute suspension of soft spheres. The diameter of the spheres is* 100 nm, *the plate-to-plate distance is* 70 nm, *and the surface area of the plates is* 1 dm$^2$. *The interaction energy between a sphere and a plate is zero if they do not overlap and* $5\times10^{-3}$ *eV if they do. The density of the spheres is* $10^{16}/\mathrm{m}^3$; *sphere–sphere interaction is negligible. Find the force acting on the plates at* 20 °C*! What is the amount of work expended if the distance between the plates is doubled isothermally?*

Like in Problem 10.2, we first calculate the partition function at $h > \sigma$, where $h$ is the width of the gap between the plates and $\sigma$ is the diameter of the soft spheres. The volume of the container $V$ can be divided into two parts. The first one contains the region where the spheres do not overlap with the plates; this corresponds to the allowed volume of Problem 10.2. The second part consists of the depletion layers of thickness $\sigma/2$ just next to the plates. Due to their softness, spheres may be present in these layers but this is associated with an increase of energy by $\phi_0 > 0$ and hence with at a lower probability. We consider $N$ soft spheres and following the same procedure as in Problem 10.2, we find that at a plate-to-plate distance $h < \sigma$ and low densities

$$\exp(-\beta F) \propto \left[V - A(\sigma + h) + A(\sigma + h)\exp(-\beta\phi_0)\right]^N,$$

where $A$ is the surface area of a single plate. By assuming that $V \gg A(\sigma + h)$, we obtain the force between the plates:

$$\mathcal{F} = -\left(\frac{\mathrm{d}F}{\mathrm{d}h}\right)_T = -\frac{Nk_BTA}{V}\left[1 - \exp(-\beta\phi_0)\right].$$

The force is attractive, its magnitude being 73 nN. It is also interesting to consider two limiting cases: For $\phi_0 \to \infty$ the spheres are hard, yielding $\mathcal{F} = -Nk_BTA/V$ like in Problem 10.2. On the other hand, for $\phi_0 \to 0$ the sphere-plate interaction vanishes and so does the depletion force between the plates.

A nonzero force is observed as long as the depletion layers at the two plates overlap, i.e., for $h < \sigma$. For $h > \sigma$, the Helmholtz free energy $F$ does not depend on $h$, which leads to $\mathcal{F} = 0$. Thus, upon doubling the distance between the plates, work against the depletion force is expended only up to $h = \sigma = 100$ nm. At a constant temperature and starting from $h' = 70$ nm we obtain

$$W = \frac{Nk_BTA}{V}\left[1 - \exp(-\beta\phi_0)\right](\sigma - h') = 2.2 \times 10^{-15}\ \mathrm{J}.$$

**Problem 10.6.**

*A pair of parallel plates is immersed in a dilute suspension of rod-like molecules. Each molecule is* 20 nm *long, the distance between the plates is* 15 nm, *and the surface area of the plates is* 1 m$^2$. *Calculate the change of force acting between the plates after a magnetic field of strength* $10^6$ A/m *is applied isothermally perpendicular to the plates! The interaction of a molecule with the magnetic field is given by the Hamiltonian* $\mathcal{H}_m = -\gamma(\mathbf{a}\cdot\mathbf{H})^2$, *where* $\mathbf{a}$ *is a unit vector along the long molecular axis and* $\mathbf{H}$ *is the magnetic field strength*; $\gamma = 10^{-34}$ Vsm$^2$/A. *One* cm$^3$ *of the suspension contains* $10^{14}$ *molecules; temperature is* 300 K.

By following the approach and notation of Problem 10.3, for $h < d$ the partition function for $N$ independent molecules can be written as

$$\exp(-\beta F) \propto \left\{\int_0^{\theta_{\min}} \left[V - A(h + d\cos\theta)\right]\exp(\alpha\cos^2\theta)\sin\theta\mathrm{d}\theta \right.$$
$$\left. + \int_{\theta_{\min}}^{\pi/2} \left[V - 2Ad\cos\theta\right]\exp(\alpha\cos^2\theta)\sin\theta\mathrm{d}\theta\right\}^N,$$

where $\alpha = \beta\gamma H^2 \approx 0.024$. Since $\alpha \ll 1$, the Boltzmann factors can be expanded to first order. By integrating over $\theta$ and assuming $V \gg Ad$, $Ah$ we first obtain $F$ and then the force:

$$\mathcal{F} = -\frac{Nk_BTA}{V}\left[1 - \frac{h}{d} + \frac{\alpha}{3}\left(1 - \frac{h^3}{d^3}\right)\right].$$

For $\alpha = 0$ (corresponding to zero field), we recover the result of Problem 10.3. If $\mathbf{H} \neq 0$, the magnitude of the attractive depletion force between the plates increases by

$$\Delta\mathcal{F} = \frac{N}{V}\frac{A\gamma H^2}{3}\left(1 - \frac{h^3}{d^3}\right) \approx 1.9\ \text{mN}.$$

For $\alpha \neq 0$ the molecules align preferentially along the field, which increases the number of molecules oriented perpendicular to the plates. As these molecules cannot enter the gap between the plates, the depletion interaction is enhanced.

### Problem 10.7.

*Using the cell approximation, estimate the difference of the Helmholtz free energies of the hexagonal and square crystal lattice of hard disks!*

In the cell approximation of a solid, each particle is assumed to move only within a cell defined by its neighbors which ensures, in a simple manner, that the neighboring particles do not overlap as dictated by hard-core repulsion between them. (Note that this condition is more restrictive than the requirements imposed by the pair interaction between disks.) The two crystal lattices in question are divided into cells using the Voronoi tessellation depicted in Fig. 10.4. The thus obtained Voronoi cells reflect the lattice symmetry; in the cubic lattice they are squares, whereas in the hexagonal

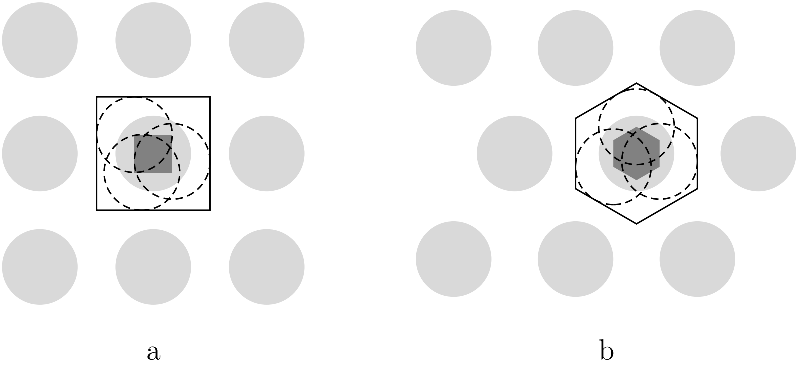

**Fig. 10.4** Voronoi tessellation shows that the cell confining a given disk is a square in the case of the square lattice (a) and a regular hexagon in the case of the hexagonal lattice (b); light gray circles represent the disks in equilibrium positions. The available surface area at the density shown is shaded in dark gray and is visibly larger in the hexagonal lattice; the densities of both lattices plotted are the same. The dashed contours depict a few possible allowed positions of a disk within its cell

lattice, they are regular hexagons. In both cases (but not in general), the shape of the two-dimensional figure defined by the locus of all possible positions of the disk center is the same as the shape of the cell itself.

We now calculate the available surface area for the square lattice. From Fig. 10.4 we deduce that it is equal to $A_a^s = (a - \sigma)^2$, where $a$ is the side of the cell and $\sigma$ is the diameter of the disk. Since each cell contains a single disk, we have $n = N/A = 1/a^2$ and thus $a = 1/\sqrt{n}$. Therefore $A_a^s = \sigma^2\left(1/\sqrt{n\sigma^2} - 1\right)^2$. The available surface area vanishes for $n\sigma^2 = 1$, which corresponds to the highest possible density of a cubic lattice. The part of the Helmholtz free energy that depends on the symmetry of the lattice is obtained from $\exp(-\beta F_s) \propto A_a^s$. By dropping the constant term $-2k_BT \ln \sigma$ which is identical in both lattices, we finally have

$$F_s = -2k_BT \ln\left(\frac{1}{\sqrt{n\sigma^2}} - 1\right).$$

In the hexagonal lattice, we also first relate the disk number density to cell size: $n = 1/2\sqrt{3}v^2$. Here $v$ is the height of each of the six equilateral triangles that constitute the cell. The available surface area is $A_a^h = \sigma^2\left(1/\sqrt{n\sigma^2} - 3^{1/4}/2^{1/2}\right)^2$. It is easy to see that $A_a^h = 0$ for $n\sigma^2 = 2/\sqrt{3} \approx 1.15$, i.e., at a density higher than for $A_a^s$.

Like in the square lattice we now obtain

$$F_h = -2k_BT \ln\left(\frac{1}{\sqrt{n\sigma^2}} - \sqrt{\frac{\sqrt{3}}{2}}\right).$$

The Helmholtz free energies of the square and the hexagonal lattice of hard disks obtained using the cell approximation are shown in Fig. 10.5. Evidently, the hexagonal lattice is more stable than the square lattice at all densities. This is also reflected

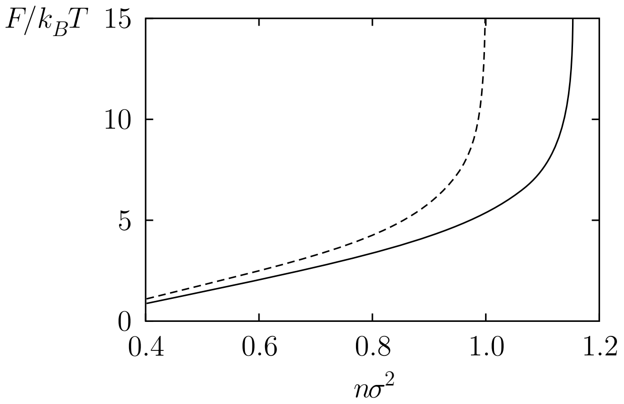

**Fig. 10.5** Helmholtz free energy of hard disks in a hexagonal and square lattice (solid and dashed line, respectively) obtained using the cell approximation plotted as a function of reduced density. The terms that do not depend on the symmetry of the lattices are omitted

in a higher value of the packing fraction of the hexagonal lattice. The packing fraction is defined as the fraction of surface area covered by the disks at the highest possible density (where neighbors touch each other). In the hexagonal lattice, the packing fraction is $\pi/2\sqrt{3} \approx 0.9069$, whereas in the square lattice it is $\pi/4 = 0.7854$. In a similar way, one can check that in three dimensions the face-centered cubic lattice and the hexagonal close-packed lattice are the most stable arrangements of hard spheres. The more sophisticated calculations that include the entropy of the correlated motion of the particles—long-wave phonons which are omitted in the cell approximation—confirm the qualitative results presented above. We also mention that the square lattice consisting of hard disks is mechanically unstable because its free energy is decreased upon an infinitesimally small shear deformation.

**Problem 10.8.**

*In a simple model of the nematic liquid crystal, we assume that the molecules are hard cylindrical rods. Estimate the density of the nematic-isotropic phase transition! Assume that in the isotropic phase the neighboring molecules are mostly perpendicular to each other, whereas in the nematic phase they are rather well aligned.*

We denote the length and the diameter of the molecules by $d$ and by $\sigma \ll d$, respectively. In order to simplify the analysis, we assume for the moment that the nematic phase is orientationally perfectly ordered so that all the molecules are aligned in the same direction. In this case, the excluded volume around each molecule that is inaccessible to the centers of mass of the neighboring molecules corresponds to a cylinder of height $2d$ and radius $\sigma$. The volume of this cylinder is $2\pi\sigma^2 d$. In a system with a particle number density $n$, an average volume belonging to a molecule is $n^{-1}$. Consequently, the available volume per molecule is given by $n^{-1} - \pi\sigma^2 d$; note that only one half of the excluded volume is assigned to each molecule (Fig. 10.6). In reality, the orientational order is partial rather than perfect as assumed above; in addition to the available volume, the partition function also includes the integral over all possible orientations of a given molecule with respect to the reference molecule, estimated by $\int d\Omega \sim 1$. At the same time, we assume that the available volume does not depend on the relative orientation of the molecules. Like in Problem 10.7, a common constant term $-k_B T \ln V_0$ is subtracted from the Helmholtz free energy per molecule, where $V_0 = \pi\sigma^2 d/4$ is the volume of one molecule. In the nematic phase one thus has

$$F_N = -k_B T \ln\left(\frac{1}{nV_0} - 4\right).$$

In the isotropic phase, the angle between two molecules is arbitrary. In this case, a rough order-of-magnitude estimate of the excluded volume can be obtained by placing the neighboring molecules at right angles. The volume around each molecule inaccessible to other molecules is an upright prism of height $d + \sigma$ and a base approximately given by a rectangle with sides $2\sigma$ and $d + \sigma$. The volume of the prism is $2\sigma(d + \sigma)^2 \approx 2\sigma d^2$. Therefore, the available volume is now given by $n^{-1} - \sigma d^2$, whereas the orientational part of the partition function is $\int d\Omega = 4\pi$. By subtracting the constant contribution $-k_B T \ln V_0$, the Helmholtz free energy per molecule in the

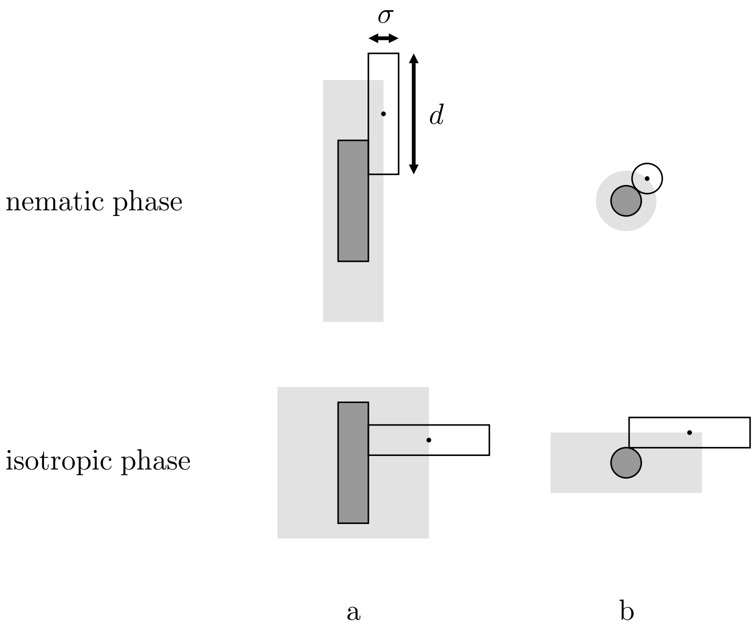

**Fig. 10.6** Excluded volume of rod-like molecules in the nematic and the isotropic phase, with the reference molecule depicted sidewise (a) and lengthwise (b). The gray shading indicates the characteristic cross sections of the excluded volume inaccessible to the centers of mass of the neighboring molecules

isotropic phase is given by

$$F_I = -k_B T \ln\left(4\pi \left(\frac{1}{nV_0} - \frac{4d}{\pi\sigma}\right)\right).$$

At the phase transition, which is achieved by varying the density just like in all other athermal systems and not by changing temperature, the Helmholtz free energies of the two phases must be equal. This condition gives an order-of-magnitude estimate of the density at the transition:

$$n_{NI} \sim \frac{1}{\sigma d^2}\,.$$

Here we assumed that $\sigma \ll d$.

Note that even this simple model can provide a sound insight into the nematic-isotropic transition. To this end, we plot the Helmholtz free energies of the nematic and of the isotropic phase as a function of $1/nV_0$, which represents the reduced volume of the system (Fig. 10.7). It turns out that for $d/\sigma < \pi$, the free energy of the isotropic phase is smaller than that of the nematic phase at any density. This means that molecules that are not sufficiently elongated cannot form a nematic phase. On the other hand, if $d/\sigma > \pi$ the free energy of the isotropic phase is smaller than that of the nematic only at low enough densities: At high densities (i.e., at low reduced volumes $1/nV_0$) the isotropic phase is replaced by the nematic phase.

Figure 10.7 also reveals that close to the reduced volume where the Helmholtz free energies of the two phases are the same, the system features a coexistence of the nematic and isotropic phase of densities determined by the Maxwell double-tangent construction. This construction also ensures mechanical equilibrium, with the pressure $p = -(\partial F/\partial V)_T$ being the same in both phases. Phase coexistence reduces the free energy compared to either single phase and guarantees mechanical stability. Namely, the isothermal compressibility of the system is inversely proportional to $\left(\partial^2 F/\partial V^2\right)_T$ and since it must be nonnegative, the Helmholtz free energy should be a convex function of volume.

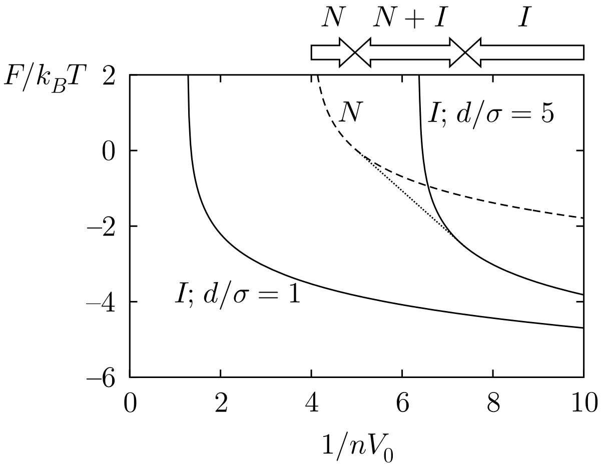

**Fig. 10.7** Helmholtz free energy of the isotropic (full lines; $d/\sigma = 1$ and 5) and of the nematic phase (dashed line) as a function of reduced volume: The former depends on the length-to-diameter ratio of the molecules, whereas the latter does not. For $d/\sigma < \pi$ the isotropic phase is more stable than the nematic phase at all densities. For $d/\sigma > \pi$, the isotropic phase is replaced by the nematic phase at a high enough density; the dotted line is the Maxwell double-tangent construction. The arrows indicate the density ranges of the nematic ($N$) and the isotropic phase ($I$) as well as their coexistence ($N + I$); all plotted for $d/\sigma = 5$

A more complete calculation of this kind was proposed by Onsager who was the first to identify the microscopic mechanism of liquid-crystalline ordering originating in the competition between the orientational and the translational entropy of molecules.

## Problem 10.9.

*When an atom escapes from the bulk to the surface of a crystal, a hole is left behind in the lattice; this is referred to as the "Schottky defect". Calculate the concentration of such defects in a crystal of silicon at* 300 °C, *given that the binding energy of an atom in the bulk exceeds that of an atom at the surface by* 2.6 eV*! The number density of silicon atoms is* $5.02 \times 10^{28}/\mathrm{m}^3$.

The energy of a crystal containing $N'$ defects is equal to $E(N') = N'w$, where $w > 0$ is the difference of binding energies at the surface and in the bulk. The entropy of a crystal consisting of $N$ atoms and $N'$ defects is approximately $S(N') = k_B \ln\big((N+N')!/N'!N!\big) \approx k_B\left[(N+N')\ln(N+N') - N'\ln N' - N\ln N\right]$, since the number of different possible arrangements of $N'$ defects onto $N+N'$ sites (occupied by either atoms or defects) is given by the binomial symbol $\binom{N+N'}{N} = (N+N')!/N'!N!$ (Fig. 10.8). This estimate is not entirely accurate as it includes also the meaningless configurations with defects at the surface. However, the fraction of such configurations is small if the defects are few, and in this case, the above approximation is justified.

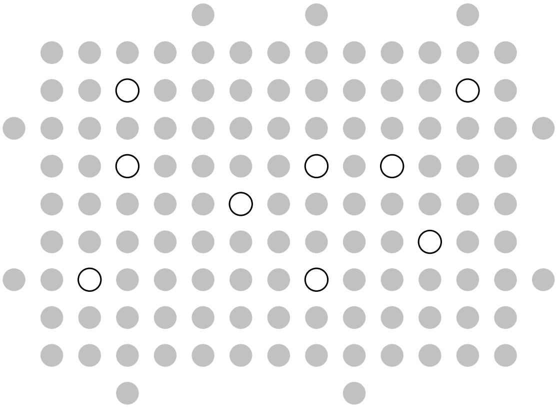

**Fig. 10.8** In a $N$-atom crystal (full circles), $N'$ Schottky defects (empty circles) can be arranged in approximately $(N+N')!/N'!N!$ ways

The free energy of a crystal containing $N'$ defects is thus

$$F(N') = N'w - k_BT\left[(N+N')\ln(N+N') - N'\ln N' - N\ln N\right].$$

The equilibrium number of defects is determined by requiring that $\left(\partial F/\partial N'\right)_T = 0$ or

$$N'(T) = \frac{N}{\exp(w/k_BT) - 1} \approx N\exp\left(-\frac{w}{k_BT}\right),$$

where we took into account that the number of defects is small. For $w = 2.6$ eV, $T = 300$ K, and $N/V = 5.02 \times 10^{28}/\mathrm{m}^3$, the number density of defects is $7.13 \times 10^5/\mathrm{m}^3$.

**Problem 10.10.**

*Analyze the temperature dependence of entropy in a two-level system consisting of independent distinguishable particles! What is the entropy of* 100 *particles at* 20 °C *if the levels are* 0.05 eV *apart?*

The phase space is determined by the number of particles occupying one of the energy levels. We use $N'$ to denote the number of particles in the upper state with energy $w$ so that the number of particles in the lower state where the energy is 0 is $N - N'$. Hence the total energy of the system is $E(N') = N'w$. The number of possible arrangements with a given energy is $\binom{N}{N'} = N!/N'!(N - N')!$ and the corresponding entropy reads

$$S(E) = k_B \ln \frac{N!}{(E/w)!\,[N - (E/w)]!}\,.$$

One can see that $S(0) = 0$ and that $S(E < Nw) = S(Nw - E)$ (Fig. 10.9): The entropy increases at energies smaller than $Nw/2$, reaches a maximum at $Nw/2$, and drops to 0 again at $E = Nw$. A non-monotonic dependence of $S(E)$ is encountered only in systems where the energy spectrum is bounded from above and where the degeneracy of energy levels does not exhibit a pronounced increase with increasing energy.

In this system, temperature is uniquely related to energy. As the system cannot perform work against its environment, the first law of thermodynamics can be written as $\mathrm{d}E = \mathrm{d}Q$ and one has $\mathrm{d}S = \mathrm{d}Q/T = \mathrm{d}E/T$. From here we obtain

$$T = \left(\frac{\mathrm{d}S}{\mathrm{d}E}\right)^{-1}.$$

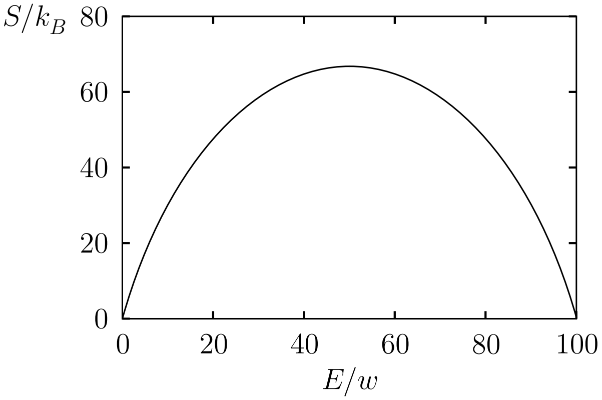

**Fig. 10.9** Entropy of a two-level system as a function of energy plotted for $N = 100$ particles. The left half of the diagram where the entropy is an increasing function of energy corresponds to positive temperatures; in the right half where the entropy decreases, the temperature is negative

Temperature thus corresponds to the inverse value of the derivative of $S(E)$. It is finite and positive at $E = 0$, exhibits a first-order vertical asymptote (a pole) at $Nw/2$, and its value at $E = Nw$ is equal and opposite to that at $E = 0$. At energies between $Nw/2$ and $Nw$ where the upper level is more populated than the lower one, the temperature is negative. (There is no need to worry about this, as temperature is merely a parameter of the Maxwell–Boltzmann distribution. In reality, a nonequilibrium inverted population can be obtained by supplying work to a thermally insulated system; for example when studying nuclear magnetic relaxation after an application of a radio-frequency pulse, or in a laser when achieving pronounced stimulated emission.)

The dependence of temperature on entropy can be explored in the limit $N, N' \to \infty$. Using the Stirling formula $\ln N'! \approx N' \ln N' - N'$ we obtain $S(E) \approx k_B\big[N \ln N - (E/w)\ln(E/w) - (N - E/w)\ln(N - E/w)\big]$, which results in

$$T \approx \frac{w}{k_B}\left[\ln\left(\frac{Nw}{E} - 1\right)\right]^{-1}.$$

Now we can explicitly express $S(T)$ and $E(T)$, which is convenient in systems that are in contact with a thermostat at a temperature $T$. The high-temperature limit of the energy is $Nw/2$, whereas the entropy for large $N$ tends to $Nk_B \ln 2$; at low temperature both energy and entropy approach 0 (Fig. 10.10). At low temperatures the system minimizes the energy so that all particles occupy the lower level, whereas at high temperatures the maximum-entropy arrangement is preferred, which leads to equal occupancy of the two levels. At finite temperatures, these two contrasting tendencies, which may also be seen as the order vs. disorder dichotomy, are combined in the Helmholtz free energy. Finally, the numerical answer: At 20 °C and the energy-level difference of 0.05 eV the entropy of 100 particles equals $39.6\,k_B = 5.47 \times 10^{-22}$ J/K.

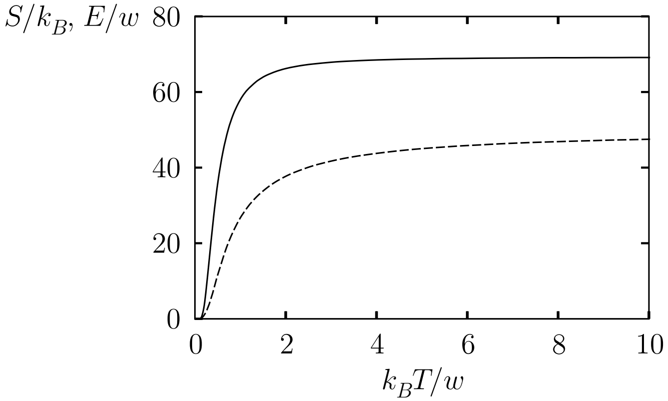

**Fig. 10.10** Entropy (full line) and energy (dashed line) of a two-level system with $N = 100$ as a function of temperature. At low temperatures, the results are not exact as we used the Stirling formula

**Problem 10.11.**

*Explore the stability of the ferromagnetic phase in two dimensions! The system is modeled by the Ising Hamiltonian with nearest-neighbor interactions only:*

$$H = -J \sum_{i,j \text{ neighbors}} s_i s_j \,.$$

*Here $J$ is the exchange integral and $s_i = \pm 1/2$ the spin component along the z-axis. What about one-dimensional systems?*

The energy of two parallel neighboring spins is equal to $-J/4$ regardless of whether they point up ($s_i = s_j = +1/2$) or down ($s_i = s_j = -1/2$). We view the paramagnetic phase as a collection of spin domains with $s_i = -1/2$ in a uniform background of spins with $s_i = +1/2$. By expressing it relative to the background state, we see that the energy consists solely of the terms corresponding to pairs of spins of opposite orientation, which lie at the domain boundaries (Fig. 10.11). Relative to the energy of parallel spins, which is $-J/4$ per pair, the energy of a boundary of length $L$ expressed in terms of the number of spins along the boundary is $E = JL/2$ as the energy of an antiparallel pair is $+J/4$.

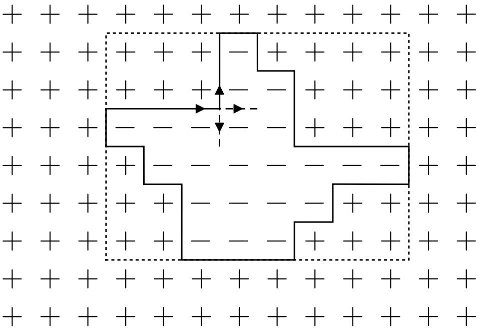

**Fig. 10.11** Ising model in 2D with a domain of spins pointing down in a background of spins pointing up. Only pairs of antiparallel spins along the domain wall (solid line) contribute to the energy of the paramagnetic phase. As the domain energy depends on its circumference rather than on its surface area, the domain plotted by the dotted line has the same energy as the one shown. At each lattice point, the domain boundary can be continued in 3 directions as shown by the arrows. This indicates that there exist approximately $3^L$ domains of same boundary circumference $L$

We now estimate the entropy of the domain boundary. For simplicity, we assume that the spins lie on a square lattice. In this case, in each lattice point, the domain boundary may be continued in three different directions. Hence the number of different domains of length $L$, all of them having the same energy $JL/2$, is equal to $3^L$ and the corresponding entropy is $k_B \ln 3^L$; here, we neglected the fact that the boundary must be a closed loop and thus our estimated entropy is too large.

By combining the energy and the entropy terms, we find that the Helmholtz free energy of a domain is

$$F_{\mathrm{2D}} = \frac{JL}{2} - k_B T \ln 3^L = \left(\frac{J}{2} - k_B T \ln 3\right) L$$

and is proportional to the domain boundary circumference $L$. We see that at temperatures above

$$T_c = (2 \ln 3)^{-1} \frac{J}{k_B} = 0.455 \frac{J}{k_B}$$

the formation of domains of arbitrary size reduces the Helmholtz free energy of the ferromagnetic phase which therefore becomes unstable. Domain formation is favorable because the magnitude of the entropic term in the free energy increases by more than the corresponding energy term once a domain is created, which results in a net decrease of Helmholtz free energy. On the other hand, below $T_c$ the domains increase the free energy so that the ferromagnetic phase is stable. Our simplified analysis certainly cannot produce an accurate estimate of the critical temperature $T_c$; its exact value is due to Onsager and reads

$$T_c = \left[2 \ln\left(\sqrt{2} + 1\right)\right]^{-1} \frac{J}{k_B} = 0.567 \frac{J}{k_B} .$$

In one dimension, only two pairs of spins contribute to the energy of a domain boundary regardless of domain size. Here, the domain energy (again calculated relative to the perfectly ordered ferromagnetic phase with all spins aligned) is equal to $J$. In a $N$-spin system, the first edge of a domain can be placed at $N-1$ sites and the second can be at the remaining $N-2$ sites. The number of domains with same energy is thus $(N-1)(N-2)/2 \sim N^2$, where the factor $1/2$ accounts for the double-counting of domains within the above scheme. It follows that

$$F_{\mathrm{1D}} = J - 2 k_B T \ln N ,$$

which approaches $-2k_B T \ln N$ in the thermodynamic limit $N \to \infty$. In one dimension, the formation of domains is favorable at all temperatures, which means that ferromagnetic order cannot exist at any $T > 0$.

**Problem 10.12.**

*In a simple two-dimensional model, a polymer is represented by a chain of segments on a square lattice. The energy of a bond between two monomers is* 0.1 eV *if the monomers are mutually perpendicular and* 0 *for a stretched-out configuration. The hairpin configuration where the angle between two consecutive segments is equal to* $\pi$ *is not allowed. Calculate the conformational part of the heat capacity of a* 100-*monomer chain at* 300 K*! Explore the high- and the low-temperature limits! The kilomolar mass of a monomer is equal to* 78 kg/kmol.

Following Problem 10.10, we first determine the size of phase space occupied by configurations with $N$ bonds and $N'$ corners (Fig. 10.12):

$$\Delta\Gamma(N') = \frac{N!}{N'!(N-N')!} 2^{N'} ,$$

where the factor of $2^{N'}$ arises because of the two degenerate perpendicular conformations that are possible for each bond. The energy of the polymer is $E = wN'$ and its entropy is $S(E) = k_B \ln \Delta\Gamma(E)$ or

$$S(E) = Nk_B \left[ \frac{E}{Nw} \ln 2 - \left(1 - \frac{E}{Nw}\right) \ln \left(1 - \frac{E}{Nw}\right) - \frac{E}{Nw} \ln \frac{E}{Nw} \right],$$

where we used the Stirling formula $\ln n! \approx n \ln n - n$. Thus the inverse temperature is $1/T = \mathrm{d}S/\mathrm{d}E = (k_B/w)\,[\ln 2 + \ln (Nw/E - 1)]$. Finally, we have $E(T) = Nw/\left[1 + \exp(w/k_BT)/2\right]$ and

$$C(T) = Nk_B \left(\frac{w}{k_BT}\right)^2 \frac{\exp(w/k_BT)/2}{\left[1 + \exp(w/k_BT)/2\right]^2} .$$

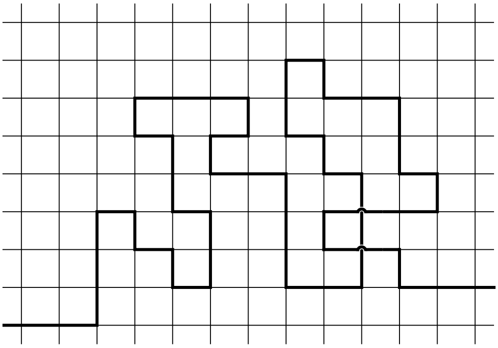

**Fig. 10.12** Lattice model of a polymer: A corner carries an energy $w$, whereas the energy of a stretched-out bond is zero. The model also allows for intersecting configurations

At low temperatures we have $C(T) \approx 2Nk_B(w/k_BT)^2 \exp(-w/k_BT)$, whereas at high temperatures, we obtain $C(T) \approx (2Nk_B/9)(w/k_BT)^2$. For $w = 0.1$ eV we obtain $c = C/(N+1)m_0 = 60.6$ J/kgK; here $m_0$ denotes the mass of a single monomer.

The same result is obtained by starting from the partition function for $N$ independent bonds where $\exp(-\beta F) = \left[1 + 2\exp(-w/k_BT)\right]^N$.

**Problem 10.13.**
*Let the interatomic interaction in a nonideal gas be given by*

$$\phi(r) = \begin{cases} \infty, & r < \sigma \\ \phi_0\,(r/\sigma - 2)\,, & \sigma \le r < 2\sigma \\ 0, & r \ge 2\sigma \end{cases} .$$

*A liter of such a gas at* 300 K *is isothermally expanded so that its volume increases by a factor of* 10. *How much heat does the gas exchange with the environment in this process? How does the result differ from that obtained with an ideal gas? What fraction of the correction originates in attractive/repulsive forces between atoms? The initial pressure is equal to* $10^7$ Pa; $\phi_0 = 10^{-3}$ eV *and* $\sigma = 0.2$ nm.

We first calculate the second virial coefficient which reads

$$B_2 = 4V_0(1 - 11\beta\phi_0/4)\,.$$

Here, we took into account that $\beta\phi_0 \ll 1$; $V_0 = \pi\sigma^3/6$. Upon reversible isothermal expansion at $T = 300$ K, the heat exchanged by the gas with the environment reads $Q = T\Delta S$, where $\Delta S$ is the change of entropy in the process. From $F = \langle E\rangle - TS$ it follows that $\Delta S = (\Delta\langle E\rangle - \Delta F)/T$ and, in turn, $Q = \Delta\langle E\rangle - \Delta F$. Now we need to calculate the changes of the internal and of the Helmholtz free energy of the gas. (Recall that in isothermal changes $\Delta F$ represents the maximal amount of work that a system can expend, the maximum corresponding to a reversible process. Therefore, the expression for $Q$ is nothing but the first law of thermodynamics.) $\langle E\rangle$ includes the kinetic and the interaction term $U_k(T)$ and $U_i(T, V)$, respectively, which are derived in Problem 9.14:

$$\langle E\rangle = U_k(T) + U_i(T, V) = U_k(T) - \frac{11N^2\phi_0 V_0}{V}\,.$$

The free energy too consists of the kinetic and the interaction term $F_k(T)$ and $F_i(T, V)$, respectively; we borrow them from Problem 9.13:

$$\begin{aligned} F &= F_k(T) + F_i(T, V) = F_k(T) - \beta^{-1}\ln Z(T, V) \\ &= F_k(T) - k_BT\left[N\ln V - \frac{4V_0N^2}{V}\left(1 - \frac{11\phi_0}{4k_BT}\right)\right]. \end{aligned}$$

Since expansion is isothermal, the kinetic terms of the energy and Helmholtz free energy remain unchanged. By collecting all terms and taking $N \approx \beta pV' = 2.4 \times 10^{24}$, we have

$$Q = T\Delta S = Nk_BT\left[\ln\frac{V}{V'} + 4V_0N\left(\frac{1}{V'} - \frac{1}{V}\right)\right] = 2.33 \times 10^4\ \mathrm{J}\,.$$

The obtained value exceeds the ideal gas result—the $\ln V/V'$ term—by 1.6%. Only repulsive forces contribute to the correction; all terms containing the constant $\phi_0$ which originates in the attractive part of the potential cancel out.

**Problem 10.14.**

*In a polymer chain, each monomer can be bonded in three ways: In the first case, its contribution to the length is* $a$, *in the second* $2a$, *and in the third* $4a$. *A stretching force of* 1 pN *is applied isothermally to a polymer consisting of* 10 *monomers. Calculate the elongation of the polymer if the temperature is* 300 K*! How much heat does it exchange with the environment? Assume that* $a = 1$ nm*!*

For generality, we denote the contribution of each monomer in the three bonding configurations to the length of the polymer by $a$, $b = 2a$, and $c = 4a$. The partition function for a $N$-monomer chain reads (Problem 9.10)

$$\exp(-\beta G) = \left[\exp(\beta a\mathcal{F}) + \exp(\beta b\mathcal{F}) + \exp(\beta c\mathcal{F})\right]^N ,$$

where $\mathcal{F}$ stands for the stretching force. The average length is then equal to

$$\langle \ell \rangle = -\left(\frac{\partial \beta G}{\partial \beta \mathcal{F}}\right)_\beta = N\frac{a\exp(\beta a\mathcal{F}) + b\exp(\beta b\mathcal{F}) + c\exp(\beta c\mathcal{F})}{\exp(\beta a\mathcal{F}) + \exp(\beta b\mathcal{F}) + \exp(\beta c\mathcal{F})} .$$

In the force-free polymer we have $\langle \ell \rangle = N(a+b+c)/3 = 23.3$ nm and in the loaded polymer at 1 pN $\langle \ell \rangle = 27.2$ nm. The elongation of the polymer is thus 3.9 nm or 16.6%.

The heat exchanged with the environment at a given temperature ($T$) is calculated from the change of entropy: $Q = T\Delta S$. In turn, the change of entropy is extracted from the changes of the average enthalpy and the Gibbs free energy, i.e., $\Delta S = \Delta(\langle H\rangle - G)/T$. The average enthalpy of the polymer is equal to

$$\langle H\rangle = \left(\frac{\partial \beta G}{\partial \beta}\right)_{\mathcal{F}} = -\mathcal{F}\langle \ell \rangle ,$$

whereas the Gibbs free energy is given by

$$G = -Nk_BT\ln\big(\exp(\beta a\mathcal{F}) + \exp(\beta b\mathcal{F}) + \exp(\beta c\mathcal{F})\big).$$

Finally we have

$$\begin{aligned} Q &= \Delta\langle H\rangle - \Delta G \\ &= -\mathcal{F}\langle \ell \rangle + Nk_BT\left[\ln\big(\exp(\beta a\mathcal{F}) + \exp(\beta b\mathcal{F}) + \exp(\beta c\mathcal{F})\big) - \ln 3\right] \\ &= -12.1\ \text{meV} . \end{aligned}$$

Upon loading, heat is released by the polymer like in the elastocaloric effect.

**Problem 10.15.**

*In a chain polymerization process, the probability of adding a new monomer onto an existing linear chain does not depend on chain length. Calculate the width of the probability distribution of the chain length at the end of the process if the average chain length has reached* $10^3$ *monomers! What is the polydispersity coefficient* $\langle n^2\rangle/\langle n\rangle^2 - 1$, *where n denotes the chain length?*

We first determine the probability distribution of chain lengths $w(n)$. We use $P$ to denote the probability of establishing a bond when a free monomer approaches an active reactive center at the end of an existing chain. The probability of observing $n$ successful bonding events after $N$ attempts (which leads to a chain consisting of $n+1$ monomers) is

$$w(n) = \frac{N!}{n!(N-n)!}\, P^n (1-P)^{N-n}\,.$$

In the above expression, one can recognize the binomial distribution. The average chain length is equal to $\langle n\rangle + 1 = NP + 1$. If we wish to grow chains of a given average length and have $P \to 0$ at the same time, the process of polymerization should be lengthy with $N \to \infty$. By keeping $\langle n\rangle = NP$ constant when taking this limit, the binomial distribution is transformed into the Poisson distribution (Fig. 10.13) and

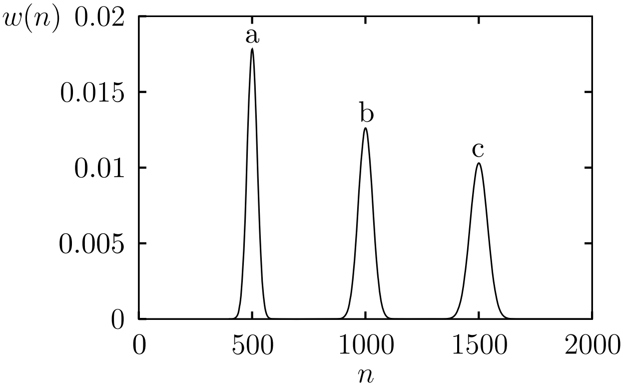

**Fig. 10.13** Probability distribution of polymer chain lengths upon chain polymerization for $\langle n\rangle = 5\times 10^2$ (a), $10^3$ (b) in $1.5\times 10^3$ (c)

$$w(n) = \frac{\langle n\rangle^n}{n!} \exp\left(-\langle n\rangle\right).$$

We replace $\langle n\rangle$ in the normalization integral $\int_0^\infty w(n)\,\mathrm{d}n = 1$ by $k\langle n\rangle$, take the derivative with respect to $k$ twice, insert $k = 1$, and obtain $\langle n^2\rangle = \langle n\rangle^2 + \langle n\rangle$. The width of the Poisson distribution at $\langle n\rangle = 10^3$ is therefore $\sqrt{\langle n^2\rangle - \langle n\rangle^2} = \sqrt{\langle n\rangle} =$ 31.6 monomers. The polydispersity coefficient is equal to

$$\frac{\langle n^2\rangle}{\langle n\rangle^2} - 1 = \frac{1}{\langle n\rangle} = 0.001$$

and decreases with increasing chain length.

**Problem 10.16.**
*The microscopic structure of rubber is similar to a network of freely jointed polymer chains. In a simple model we assume that all chains are of same length and that there are no chain entanglements between the crosslinks. In this case, the probability distribution of chain end-to-end distances $r$ is Gaussian*

$$w(r) = \left(\frac{3}{2\pi N a^2}\right)^{3/2} \exp\left(-\frac{3r^2}{2Na^2}\right),$$

*where $a$ is a monomer length and $N$ is the number of monomers between crosslinks on the same chain. Calculate the Young's modulus of rubber, assuming that the deformation is affine at the microscopic level and that the sample is incompressible! A sample of volume of $10\,\mathrm{cm}^3$ consists of $10^{23}$ monomers, $N = 100$, and temperature is 300 K!*

Given that in this model the chains are assumed to be ideally flexible (so that their conformational internal energy is neglected), the elasticity of rubber is entirely entropic. The Helmholtz free energy of a single chain in an undeformed rubber sample is equal to

$$F' = -TS = -k_B T \ln w(r) = F_0(T) + \frac{3k_B T\, r^2}{2Na^2}\,,$$

where $F_0(T)$ is a temperature-dependent constant. We assume that the rubber is uniaxially stretched along the $z$-axis and we denote the relative stretching factor by $\lambda$. Because of the constant-volume constraint the sample contracts along the $x$- and $y$-axis by a factor of $\lambda^{-1/2}$ (Fig. 10.14). Upon deformation, the initial value of $r^2 = x^2 + y^2 + z^2$ for a single chain is changed and reads $(x^2 + y^2)/\lambda + \lambda^2 z^2$. The corresponding distribution $w(r)$ changes too as the deformation affects the number of available configurations between chain ends, which decreases with increasing end-to-end distance and vice versa. The Helmholtz free energy of a deformed chain reads

$$F = F_0(T) + \frac{3k_B T}{2Na^2}\left(\frac{x^2 + y^2}{\lambda} + \lambda^2 z^2\right).$$

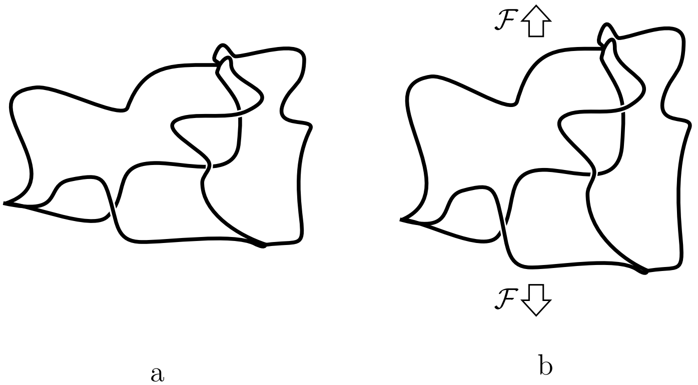

**Fig. 10.14** Schematic depiction of polymer chains in rubber in the undeformed state (**a**) and in a uniaxially stretched sample (**b**). The external load changes the contours of the chains, thereby increasing the Helmholtz free energy

The deformation free energy of the entire sample is given by the difference $F_d = F - F'$ averaged over the $\nu = M/N$ chains in the sample (here $M$ is the total number of monomers)

$$F_d = \frac{3\nu k_B T}{2Na^2}\left[\left(\lambda^{-1}-1\right)\left(\langle x^2\rangle + \langle y^2\rangle\right) + \left(\lambda^2 - 1\right)\langle z^2\rangle\right].$$

The averages $\langle x^2\rangle$, $\langle y^2\rangle$, and $\langle z^2\rangle$ must be calculated in an undeformed sample, which is isotropic so that $\langle x^2\rangle = \langle y^2\rangle = \langle z^2\rangle$. Furthermore,

$$\langle r^2\rangle = \langle x^2\rangle + \langle y^2\rangle + \langle z^2\rangle = \int_0^\infty r^2 w(r)\, 4\pi r^2\, \mathrm{d}r = Na^2$$

so that $\langle x^2\rangle = \langle y^2\rangle = \langle z^2\rangle = Na^2/3$. Finally we obtain

$$F_d = \frac{\nu k_B T}{2}\left(\lambda^2 + \frac{2}{\lambda} - 3\right),$$

which has a minimum at $\lambda = 1$: This represents the isotropic state where the entropy of the polymer chains, which lack any orientational order on average, is largest.

The external stretching force needed to deform the rubber is equal to

$$\mathcal{F} = \left(\frac{\partial F_d}{\partial z}\right)_{T,V} = \frac{1}{\ell}\left(\frac{\partial F_d}{\partial \lambda}\right)_{T,V} = \frac{\nu k_B T}{\ell}\left(\lambda - \lambda^{-2}\right),$$

where $\ell$ is the length of the undeformed sample measured along the $z$-axis; the dependence of $\mathcal{F}$ on $\lambda$ is shown in Fig. 10.15. The isothermal Young's modulus is thus

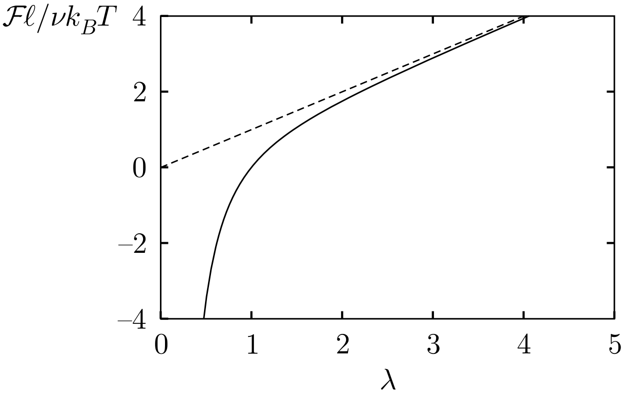

**Fig. 10.15** Dependence of the stretching force $\mathcal{F}$ in rubber on $\lambda$ (solid line). The stretching force is equal to 0 for $\lambda = 1$, corresponding to the undeformed sample. The sign of the force is negative in compressed states where $\lambda < 1$ and positive in stretched states where $\lambda > 1$. The dashed line represents the large-deformation limit where $\mathcal{F}(\lambda)$ is a linear function

$$E_T = \frac{1}{A}\left(\frac{\partial \mathcal{F}}{\partial \lambda}\right)_{TV} = \nu^* k_B T\left(1 + \frac{2}{\lambda^3}\right).$$

Here $A$ is the area of the cross section perpendicular to the force in the undeformed sample, whereas $\nu^* = \nu/A\ell$ is the volumetric density of chains. Unlike in solids, the Young's modulus of rubber increases with temperature. For $\lambda \gg 1$, $\mathcal{F}$ is a linear function of $\lambda$ and we obtain

$$E_T \approx \frac{M k_B T}{N V_0} = 4.14 \times 10^5\ \mathrm{N/m^2}.$$

Here $V_0 = A\ell$ is the volume of the sample.

The assumption that the distribution $w(r)$ is Gaussian is valid only at moderate deformations, i.e., for $\lambda$ close to unity where the chains are not fully stretched-out. The validity of this assumption is restricted by the condition $\lambda\langle r^2\rangle^{1/2} \ll Na$, which gives $\lambda \ll \sqrt{N} = 10$. Lastly, in the above analysis, we neglected the fluctuations of the crosslinks as well as the chain entanglements between crosslinks. Despite these approximations, the predictions of the model agree with experiments rather well.

**Problem 10.17.**

*The volume occupied by a polymer molecule in a solvent is quantified by the average* $\langle r^2\rangle \propto N^{2\rho}$, *where* $r$ *stands for the distance between its ends,* $N$ *is the number of monomers in the chain, and* $\rho$ *is a characteristic exponent. In the so-called good solvents, the flexibility of an ideal freely jointed chain is restricted primarily by* *the repulsive steric interaction between the monomers. Calculate the value of the exponent $\rho$ for this case! Hint: Assume that the energy density due to steric interaction is proportional to the square of monomer concentration, whereas the entropic term in the Helmholtz free energy is the same as in the freely jointed chain!*

In Problem 10.16 we found that for an ideally flexible freely jointed chain $\langle r^2 \rangle \propto N$, implying that $\rho = 1/2$. The part of the corresponding entropic Helmholtz free energy that depends on chain length is proportional to $\langle r^2 \rangle / N$. The repulsive steric interaction energy is proportional to the number of monomer pairs and can be estimated by

$$U_s \sim \frac{v}{2} \left( \frac{N}{V_p} \right)^2 V_p \, .$$

The expression in the brackets represents the concentration of monomers, $V_p \propto \langle r^2 \rangle^{d/2}$ is the volume occupied by a polymer in $d$ dimensions, the constant $v$ is related to the strength of the steric interaction, and the factor $1/2$ is there so as to count each pair of monomers only once. (This is known as the mean-field Flory theory.) After combining the elastic energy of the freely jointed chains and $U_s$ one obtains

$$F \propto c_1 \frac{\langle r^2 \rangle}{N} + c_2 \frac{N^2}{\langle r^2 \rangle^{d/2}} \, ,$$

where $c_1$ and $c_2$ are positive constants. The two terms compete with each other: Entropic elasticity favors short end-to-end distances, whereas steric repulsion is smallest at large $r$. In equilibrium one has $\mathrm{d}F / \mathrm{d} \langle r^2 \rangle^{1/2} = 0$, which gives

$$\langle r^2 \rangle^{1/2} \propto N^{3/(d+2)} \, .$$

We calculated the so-called Flory exponent $\rho_F = 3/(d + 2)$ that is equal to $3/5$ in three dimensions, which is larger than the corresponding result for an ideal chain. This is an expected result: The volume occupied by a chain of monomers that avoid each other increases faster with increasing chain length than that of an ideally flexible chain. It turns out that the exponent $\rho$ is a universal quantity. The exact value of the exponent for self-avoiding random trajectories is 0.588, which is quite close to the above value and agrees with experiments. However, we stress that Flory's simple approach works because of an accidental cancelation of errors: By disregarding the correlations along the chain, it overestimates the monomer–monomer repulsion but the elastic free energy of the chains described by the ideal chain model is overestimated too.

The exponent $\rho$ also appears in Problems 8.10 and 8.11. Although the chains considered in these two Problems are not ideally flexible, their behavior is similar to that of flexible chains since $\rho = 1/2$; it is only the numerical factor in the expression $\langle r^2 \rangle \propto N$ that is different. The reason for the difference between $\rho$ and $\rho_F$ is the absence of the requirement that the different sections of the same chain avoid each other.

**Problem 10.18.**

*A deoxyribonucleic acid (DNA) molecule can be represented by a long zipper, where the interlocking teeth correspond to nucleotide pairs. In each nucleotide pair, the energy of the open state exceeds that of the closed state by $w > 0$. A given nucleotide pair can be in the open state only if all other pairs between that pair and the end of the molecule are also open just like in a zipper. (Assume that the zipper can be opened from one end only.) Calculate the average number of the open nucleotide pairs in a DNA molecule at a given temperature $T$!*

First we focus on a single isolated DNA molecule consisting of $n$ nucleotide pairs. The state of the molecule is fully specified by the number of open nucleotide pairs $k$, where $0 \leq k \leq n$; the corresponding energy is $E_k = kw$. The partition function reads

$$\exp(-\beta F) = \sum_{k=0}^{n} \exp(-\beta E_k) = \frac{1-\exp\big(-(n+1)\beta w\big)}{1-\exp(-\beta w)} ,$$

where, in the last step, we evaluated a finite geometric sum. (We recognize that the model is equivalent to a spin in an external magnetic field and, if $n \to \infty$, also to the quantum harmonic oscillator discussed in Problems 11.10 and 11.1, respectively.) The average number of open pairs are related to the average energy by $\langle k\rangle = \langle E\rangle/w$, where

$$\langle E\rangle = \frac{\mathrm{d}\beta F}{\mathrm{d}\beta} = w\left[\frac{1}{\exp(\beta w)-1} - \frac{n+1}{\exp\big((n+1)\beta w\big)-1}\right] .$$

In a very long chain with $n \to \infty$ the second term is negligible and we obtain $\langle k\rangle = 1/\big(\exp(\beta w)-1\big)$. For $w = 0.2\,\mathrm{eV}$ and $T = 300\,\mathrm{K}$, we have $\langle k\rangle = 4.4 \times 10^{-4} \ll 1$: At room temperature, a DNA molecule is not expected to open up spontaneously.

Alternatively, the average number of open pairs $\langle k\rangle$ can be derived by considering a system of $N$ noninteracting DNA molecules, each containing $n$ nucleotide pairs. Because a given molecule can occupy any of the $n+1$ energy levels $E_k$, this setup can be regarded as a $n+1$-level system, which may be viewed as a generalization of the two-level system from Problem 10.10. In this case, the microstate of the system is determined by specifying the number of open nucleotides for each molecule. The energy of such a microstate is given by $E = \sum_{k=0}^{n} N_k E_k$, where $N_k$ is the number od DNA molecules with $k$ nucleotides open. There exist

$$\Delta\Gamma(E) = \frac{N!}{N_0!N_1!\cdots N_n!}$$

different microstates with the same energy $E$ (where we assume that the molecules are distinguishable), with $N = \sum_{k=0}^{n} N_k$. In equilibrium at fixed temperature, the Helmholtz free energy must be minimized. By making use of the Boltzmann entropy formula, we find that

$$F = E - k_B T \ln \Delta\Gamma(E) = \sum_{k=0}^{n} N_k\big(E_k + k_B T \ln N_k\big) - N k_B T \ln N ,$$

where we assumed that $N_k \gg 1$ and resorted to the Stirling formula. The equilibrium (average) values of $N_k$ are found by setting

$$\left(\frac{\partial F}{\partial N_k}\right)_{T,N_{j\neq k}} = 0\,.$$

Note that before evaluating the derivatives, one of the $N_k$s in the expression for $F$ has to be replaced by $N_j = N - \sum_{k\neq j} N_k$ to ensure that the total number of molecules is conserved. We obtain

$$\frac{\langle N_k\rangle}{N} = \frac{\exp\left(-\beta E_k\right)}{\sum_{i=0}^{n}\exp\left(-\beta E_i\right)}\,,$$

which represents the probability of finding a molecule with $k$ nucleotides open. (Here we rederived the canonical probability distribution.) By definition, the average energy per molecule is given by

$$\langle E\rangle = \frac{\sum_{k=0}^{n} E_k\langle N_k\rangle}{N} = \frac{\sum_{k=0}^{n} E_k \exp\left(-\beta E_k\right)}{\sum_{k=0}^{n}\exp\left(-\beta E_k\right)}\,.$$

The sum in the numerator is calculated by taking the derivative of the geometric sum in the denominator with respect to the parameter $-\beta$, which leads to the same expression for $\langle E\rangle$ as above.

# Chapter 11
# Quantum Canonical Ensemble

**Problem 11.1.**
*Calculate the Helmholtz free energy, average energy, entropy, and the heat capacity of a quantum harmonic oscillator!*

The energy levels of the harmonic oscillator are equidistant,

$$E(n) = \left(n + \frac{1}{2}\right)\hbar\omega\,,$$

and nondegenerate. The partition function is a geometric series:

$$\begin{aligned}\exp\left(-\beta F\right) &= \sum_{n=0}^{\infty}\exp\left(-\left(n+\frac{1}{2}\right)\frac{T_{\rm vib}}{T}\right)\\ &= \frac{\exp\left(-T_{\rm vib}/2T\right)}{1-\exp\left(-T_{\rm vib}/T\right)}\\ &= \frac{1}{2\,\sinh\left(T_{\rm vib}/2T\right)}\,,\end{aligned}$$

where $T_{\rm vib} = \hbar\omega/k_B$ is a characteristic temperature. The Helmholtz free energy reads

$$F = \hbar\omega\left[\frac{1}{2} + \frac{T}{T_{\rm vib}}\ln\left(1-\exp\left(-\frac{T_{\rm vib}}{T}\right)\right)\right],$$

and the average energy is

$$\langle E\rangle = \hbar\omega\left[\frac{1}{2} + \frac{1}{\exp\left(T_{\rm vib}/T\right)-1}\right].$$

Here, the second term in the square brackets represents the average quantum number $\langle n\rangle$, i.e., the average occupation number.

G. Skačej and P. Ziherl, *Solved Problems in Thermodynamics and Statistical Physics*, https://doi.org/10.1007/978-3-030-27661-4_11

The entropy of the harmonic oscillator is

$$S = \frac{\langle E\rangle - F}{T} = k_B \left[ \frac{T_{\mathrm{vib}}/T}{\exp\left(T_{\mathrm{vib}}/T\right) - 1} - \ln\left(1 - \exp\left(-\frac{T_{\mathrm{vib}}}{T}\right)\right)\right],$$

and the heat capacity reads

$$C = k_B \left[\frac{T_{\mathrm{vib}}/2T}{\sinh(T_{\mathrm{vib}}/2T)}\right]^2.$$

In Fig. 11.1, all of the above quantities are plotted against temperature.

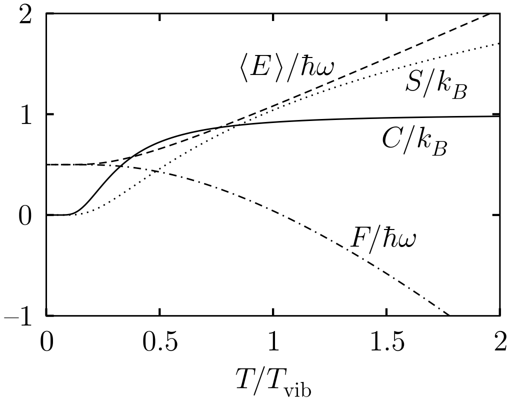

**Fig. 11.1** Quantum harmonic oscillator: Helmholtz free energy, average energy, entropy, and heat capacity plotted as functions of temperature

**Problem 11.2.**
*Explore the temperature dependence of the heat capacity of copper at high temperatures by treating lattice oscillations using the Einstein model where solid copper is represented by independent harmonic oscillators at a fixed frequency of* $4 \times 10^{13}$/s*! What is the deviation of the heat capacity from its high-temperature limit at* 500 K*? The kilomolar mass of copper is* 64 kg/kmol.

At high temperatures, the partition function of a single one-dimensional quantum harmonic oscillator (derived in Problem 11.1) can be expanded in Taylor series:

$$\exp(-\beta F) = \frac{1}{2\sinh(T_E/2T)} \approx \frac{T}{T_E}\left[1 - \frac{1}{24}\left(\frac{T_E}{T}\right)^2 + \ldots\right];$$

here $T_E = \hbar\omega_E/k_B$. This gives

$$\begin{aligned}\langle E\rangle &\approx -k_B T^2 \frac{\mathrm{d}}{\mathrm{d}T}\left[-\ln\frac{T}{T_E} + \frac{1}{24}\left(\frac{T_E}{T}\right)^2 + \ldots\right] \\ &= k_B T + \frac{1}{12}\frac{k_B T_E^2}{T} + \ldots\end{aligned}$$

In three dimensions, the number of independent oscillators per unit mass is $3N_A/M = 3R/k_B M$, where $M$ denotes the kilomolar mass, and the heat capacity is given by

$$c_V = \frac{3R}{M}\left[1 - \frac{1}{12}\left(\frac{T_E}{T}\right)^2 + \ldots\right].$$

At 500 K, the heat capacity of copper with $T_E = 304$ K is smaller than the Dulong–Petit result $3R/M \approx 390$ J/kgK by 12 J/kgK.

**Problem 11.3.**
*The energy spectrum of a particle in the Morse potential*

$$\phi(r) = D_E\left[1 - \exp\bigl(-\alpha(r - r_E)\bigr)\right]^2$$

*is given by*

$$E(n) = \left[\left(n + \frac{1}{2}\right) - x\left(n + \frac{1}{2}\right)^2\right]\hbar\omega\,,$$

*where* $\omega = \sqrt{2D_E\alpha^2/m}$ *is the frequency corresponding to the transition between the ground state and the first excited state (m denotes the mass of the particle), and* $x = \hbar\omega/4D_E$ *is the anharmonicity. Use this model to calculate the average vibrational energy of a bond in the ammonia molecule at* 4000 K*, given that* $\omega = 1.8 \times 10^{14}\ \mathrm{s}^{-1}$ *and* $x = 0.01$*!*

Anharmonicity makes the spectrum non-equidistant: The energy difference between two neighboring levels decreases with increasing $n$ and drops to 0 at

$$n_{\max} = \frac{1-2x}{2x} \approx \frac{1}{2x}\,;$$

here we assumed that anharmonicity is small. The spectrum of the Morse anharmonic oscillator is thus limited since the states with $n > n_{\max}$ are irrelevant in the present context (Fig. 11.2).

At low temperatures when the oscillator is close to its ground state, $\langle n\rangle \ll n_{\max}$, the effect of a weak anharmonicity is small. Therefore, the anharmonic factors in the partition function $\exp(-\beta F) = \sum_{n=0}^{n_{\max}} \exp\bigl(-\beta E(n)\bigr)$ can be expanded and the upper bound of the integral pushed to infinity:

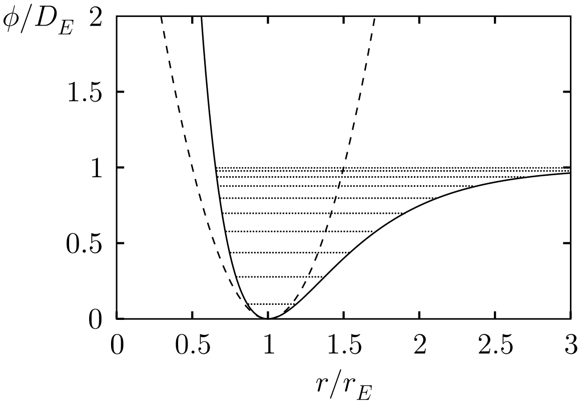

**Fig. 11.2** Morse potential for $\alpha = 2/r_E$ (solid line) and its harmonic approximation (dashed line). Also shown are the energy levels for $x = 0.05$ (dotted lines); at this anharmonicity there exist 10 bound states

$$\begin{aligned}\exp(-\beta F) &\approx \sum_{n=0}^{\infty} \exp\left(-a\left(n+\frac{1}{2}\right)\right)\left[1 + xa\left(n+\frac{1}{2}\right)^2\right]\\ &= \exp\left(-\frac{a}{2}\right)\sum_{n=0}^{\infty}\exp(-an)\left[\left(1+\frac{xa}{4}\right) + xan + xan^2\right],\end{aligned}$$

where $a = \beta\hbar\omega$. The sums $\sum_{n=0}^{\infty} n\exp(-an)$ and $\sum_{n=0}^{\infty} n^2\exp(-an)$ are evaluated by differentiating the geometric series $\sum_{n=0}^{\infty}\exp(-an) = \exp a/(\exp a - 1)$ with respect to $a$, which gives $\exp a/(\exp a - 1)^2$ and $(\exp a + 1)\exp a/(\exp a - 1)^3$, respectively. By taking into account that $x \ll 1$ we have

$$\beta F \approx -\ln\left(\frac{\exp(a/2)}{\exp a - 1}\right) - xa\left[\frac{1}{4} + \frac{1}{\exp a - 1} + \frac{\exp a + 1}{(\exp a - 1)^2}\right]$$

and as $\langle E\rangle = \mathrm{d}\beta F/\mathrm{d}\beta = \hbar\omega\mathrm{d}\beta F/\mathrm{d}a$ we find that

$$\begin{aligned}\langle E\rangle = &\left[\left(\frac{1}{2} + \frac{1}{\exp a - 1}\right)\right.\\ &\left. + x\frac{1 + (5+8a)\exp a - (5-8a)\exp(2a) - \exp(3a)}{4(\exp a - 1)^3}\right]\hbar\omega\,.\end{aligned}$$

The first term in the brackets is the average energy of the harmonic oscillator (Problem 11.1), whereas the second one is the anharmonic correction.

The numerical result is $\langle E\rangle = 3.12\,\hbar\omega = 5.89 \times 10^{-20}$ J, which is rather close to the energy $\hbar\omega/2$ and still quite far from the upper limit of the spectrum of bound states lying slightly below $25\,\hbar\omega$. If the potential were harmonic, the corresponding result would read $\langle E\rangle = 2.95\,\hbar\omega = 5.57\times 10^{-20}$ J. It is easy to see that the above approach is equivalent to the one used in solving Problem 8.13.

**Problem 11.4.**
*An electron is confined to a cubic cavity which acts as an infinite potential well. Calculate the relative variance of the energy of the electron at* 3 K*! The side of the cavity is* 30 nm.

The energy spectrum of a particle in a three-dimensional infinite potential well is given by

$$E(n_1,n_2,n_3) = \left(n_1^2+n_2^2+n_3^2\right)\frac{h^2}{8mL^2}\,,$$

where $m$ is the electron mass, $L$ is the side of the cavity, and the quantum numbers $n_1, n_2, n_3$ are all positive. The characteristic temperature $T_{\text{trans}} = h^2/8mL^2k_B$ is equal to 4.89 K, which suggests that at 3 K the sum in the partition function converges rather rapidly. By taking into account the degeneracies of the ground state and the first excited state (1 and 3, respectively), we have

$$\begin{aligned}\exp(-\beta F) &= \sum_{n_1,n_2,n_3=1}^{\infty}\exp\left(-\left(n_1^2+n_2^2+n_3^2\right)\frac{T_{\text{trans}}}{T}\right)\\ &\approx \exp\left(-3\frac{T_{\text{trans}}}{T}\right)+3\exp\left(-6\frac{T_{\text{trans}}}{T}\right)+\ldots\end{aligned}$$

If we include one more term of the partition function, the result changes by a mere 0.017%.

The average energy reads $\langle E\rangle = 3k_BT_{\text{trans}} + 9k_BT_{\text{trans}}\exp(-3T_{\text{trans}}/T)$, whereas the heat capacity is $C = 27k_B\,(T_{\text{trans}}/T)^2\exp(-3T_{\text{trans}}/T)$. The fluctuations of the energy around the average are given by $\sigma_E = \sqrt{k_BT^2C} = 3\sqrt{3}k_BT_{\text{trans}}\exp(-3T_{\text{trans}}/2T)$ so that

$$\frac{\sigma_E}{\langle E\rangle} = \frac{\sqrt{3}\exp(-3T_{\text{trans}}/2T)}{1+3\exp(-3T_{\text{trans}}/T)} = 0.15\,.$$

**Problem 11.5.**
*Calculate the average energy and the heat capacity of a quantum-mechanical rotator!*

The energy levels of a rotator are given by

$$E(j) = j(j+1)\frac{\hbar^2}{2I}\,,$$

where $I$ is the moment of inertia and $j$ is the angular momentum; the degeneracy of the levels is $(2j+1)$. Again one can introduce a characteristic temperature

$T_{\rm rot} = \hbar^2/2Ik_B$. The sum in the partition function

$$\exp(-\beta F) = \sum_{j=0}^{\infty}(2j+1)\exp\left(-j(j+1)\frac{T_{\rm rot}}{T}\right)$$

cannot be calculated in a closed form. However, at low temperatures it suffices to consider just a few largest terms of the sum—at least two, or else the system is locked in a single state. Therefore

$$\exp(-\beta F) \approx 1 + 3\exp\left(-2\frac{T_{\rm rot}}{T}\right)$$

so that $\langle E\rangle \approx 6k_BT_{\rm rot}\exp(-2T_{\rm rot}/T)/\left[1+3\exp(-2T_{\rm rot}/T)\right]$ and

$$C(T \ll T_{\rm rot}) \approx 12k_B\left(\frac{T_{\rm rot}}{T}\right)^2\exp\left(-2\frac{T_{\rm rot}}{T}\right).$$

At high temperatures, $\langle j\rangle \gg 1$ so that the sum in the partition function can be replaced by an integral:

$$\exp(-\beta F) \approx \int_0^{\infty}\exp\left(-u\frac{T_{\rm rot}}{T}\right)\mathrm{d}u = \frac{T}{T_{\rm rot}},$$

where $u = j(j+1)$. Thus $\langle E\rangle = k_BT$ and

$$C(T \gg T_{\rm rot}) = k_B.$$

The asymptotic temperature dependence of the heat capacity requires more effort. The above approximation of the partition function can be improved using the Euler–MacLaurin formula

$$\sum_{n=0}^{\infty}f(n) = \int_0^{\infty}f(x)\mathrm{d}x + \frac{1}{2}f(0) - \frac{1}{12}f'(0) + \frac{1}{720}f'''(0) - \frac{1}{30240}f^{(V)}(0) + \ldots,$$

where in the present case $f(j) = (2j+1)\exp\bigl(-j(j+1)T_{\rm rot}/T\bigr)$. To include corrections of the order of $\mathcal{O}(1)$ and $\mathcal{O}(T_{\rm rot}/T)$, we must retain the terms containing $f(0)$, $f'(0)$, and $f'''(0)$. This leads to

$$\exp(-\beta F) \approx \frac{T}{T_{\rm rot}} + \frac{1}{3} + \frac{T_{\rm rot}}{15T} + \ldots$$

so that $\langle E\rangle = k_B T - k_B T_{\mathrm{rot}}/3 - k_B T_{\mathrm{rot}}^2/45T + \dots$ and

$$C(T \gg T_{\mathrm{rot}}) = k_B\left[1 + \frac{1}{45}\left(\frac{T_{\mathrm{rot}}}{T}\right)^2 + \dots\right].$$

At high temperatures, the heat capacity of the rotator decreases, which indicates that $C$ is a non-monotonic function of temperature. This can be verified by carrying out a full numerical calculation (Fig. 11.3).

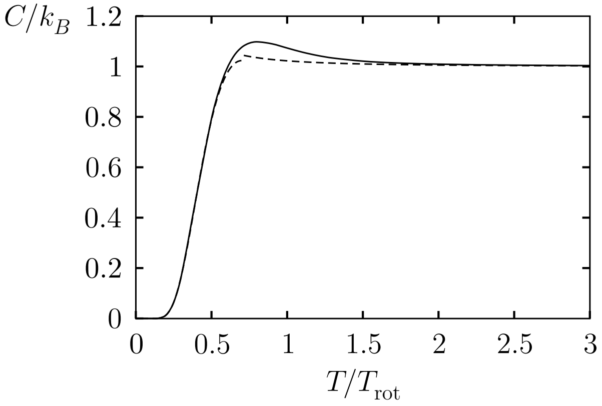

**Fig. 11.3** Heat capacity of a rotator (solid line) increases exponentially at low temperatures, reaches a maximum at $T/T_{\mathrm{rot}} = 0.807$, and approaches the classical value of $k_B$ at high temperatures. The low-temperature approximation agrees very well with the exact result, whereas the high-temperature approximation fares somewhat worse although it does indicate the existence of a maximum (dashed lines)

## Problem 11.6.

*Calculate the heat capacities of orthohydrogen and parahydrogen at* 20 K*! The angular momentum of the hydrogen molecule is* $4.7 \times 10^{-48}$ kgm$^2$.

Since the characteristic temperature $T_{\mathrm{rot}} = \hbar^2/2Ik_B$ is 86 K, we are interested in the low-temperature behavior of the two spin isomers of hydrogen. First, we realize that upon particle exchange, the proton wavefunction must be antisymmetric as a whole because protons are fermions. In parahydrogen, the spin part of the wavefunction is a singlet and hence antisymmetric, and thus the spatial (i.e., the rotator) part of the wavefunction must be symmetric. This means that $j$ must be even:

$$\exp\left(-\beta F_{\mathrm{para}}\right) = 1 + 5\exp\left(-6\frac{T_{\mathrm{rot}}}{T}\right) + \dots$$

The heat capacity of parahydrogen is

$$C_{\text{para}} = 180k_B \left(\frac{T_{\text{rot}}}{T}\right)^2 \exp\left(-6\frac{T_{\text{rot}}}{T}\right) + \ldots$$
$$\approx 2.08 \times 10^{-8} k_B = 2.87 \times 10^{-31}\ \text{J/K}\,.$$

In orthohydrogen the spin part of the wavefunction is a triplet and hence symmetric, whereas the spatial part is antisymmetric with odd $j$. At low temperatures the partition function is given by

$$\exp\left(-\beta F_{\text{ortho}}\right) = 3\left[3\exp\left(-2\frac{T_{\text{rot}}}{T}\right) + 7\exp\left(-12\frac{T_{\text{rot}}}{T}\right) + \ldots\right],$$

where the factor of 3 in front of the square bracket is due to the threefold spin degeneracy of the wavefunctions. The heat capacity is

$$C_{\text{ortho}} = \frac{700}{3} k_B \left(\frac{T_{\text{rot}}}{T}\right)^2 \exp\left(-10\frac{T_{\text{rot}}}{T}\right) + \ldots$$
$$\approx 9.13 \times 10^{-16} k_B = 1.26 \times 10^{-38}\ \text{J/K}\,.$$

**Problem 11.7.**
*What is the equilibrium composition of the orthohydrogen/parahydrogen mixture at 35 K?*

The concentrations of orthohydrogen and parahydrogen in an equilibrium mixture are proportional to their respective partition functions, which are the sums of the relative probabilities of finding a hydrogen molecule in a given rotator state. Therefore

$$\frac{N_{\text{ortho}}}{N_{\text{para}}} = \frac{3\left[3\exp\left(-2T_{\text{rot}}/T\right) + 7\exp\left(-12T_{\text{rot}}/T\right) + \ldots\right]}{1 + 5\exp\left(-6T_{\text{rot}}/T\right) + \ldots}$$
$$\approx 9\exp\left(-2\frac{T_{\text{rot}}}{T}\right),$$

which is equal to 0.066 at 35 K, since $T_{\text{rot}} = 86$ K. Thus the orthohydrogen fraction is $x_{\text{ortho}} = N_{\text{ortho}}/(N_{\text{ortho}} + N_{\text{para}}) = 0.062$.

At high temperatures, the symmetric and the antisymmetric rotator states are occupied with equal probabilities. The ratio of the spin isomer fractions then depends only on the spin degeneracy and is equal to 3 : 1 so that the orthohydrogen share is 0.75 (Fig. 11.4).

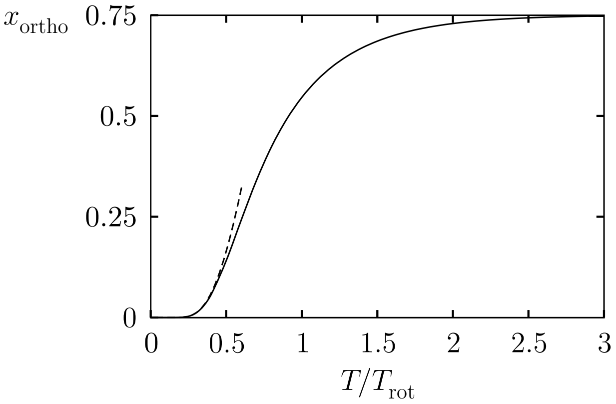

**Fig. 11.4** Temperature dependence of the orthohydrogen fraction in an equilibrium mixture of molecular hydrogen spin isomers (solid line). The simplest low-temperature approximation (dashed line) agrees well with the exact result: At $T/T_{\mathrm{rot}} = 0.3$ the relative error is only slightly larger than 1%

### Problem 11.8.

*The characteristic temperatures of the rotational and the vibrational states of a nitrogen oxide* (NO) *molecule are* 2.47 K *and* 2740 K, *respectively. Calculate the heat capacity of* NO *at* 300 K*! In the analysis, include the contribution of the first excited electronic state which is* 0.15 eV *above the ground state; the degeneracy of both states is* 2.

As the characteristic rotator temperature is only 2.47 K, the heat capacity of the rotational degrees of freedom at 300 K is equal to $C_{\mathrm{rot}} = k_B$ in agreement with the solution to Problem 11.5. The heat capacity due to the translational motion in a rarefied gas with $N/V \to 0$ is $C_{\mathrm{trans}} = 3k_B/2$ at all temperatures, whereas the heat capacity due to the vibrational motion is marginal at room temperature since the corresponding characteristic temperature is much higher ($T_{\mathrm{vib}} = 2740$ K). As shown in Problem 11.1, for $T \ll T_{\mathrm{vib}}$ one has $C_{\mathrm{vib}} = k_B\,(T_{\mathrm{vib}}/T)^2 \exp{(-T_{\mathrm{vib}}/T)} = 0.009\,k_B$. The heat capacity due to the excited electronic state is also rather modest because the relative occupancy of this state is rather small, amounting to $\exp{(-\Delta E/k_BT)} = 0.003$. The corresponding partition function reads $\exp{(-\beta F_{\mathrm{el}})} \approx 2\,[1+ \exp{(-\Delta E/k_BT)}]$, and the resulting electronic heat capacity is equal to $C_{\mathrm{el}} = k_B\,(T_{\mathrm{el}}/T)^2 \exp{(-T_{\mathrm{el}}/T)} = 0.102\,k_B$, where $T_{\mathrm{el}} = \Delta E/k_B = 1740$ K. In all, the total heat capacity is

$$C = C_{\mathrm{trans}} + C_{\mathrm{rot}} + C_{\mathrm{vib}} + C_{\mathrm{el}} = 2.611\,k_B = 3.603 \times 10^{-23}\ \mathrm{J/K}\,.$$

### Problem 11.9.

*The energy spectrum of a planar rotator is given by* $E_j = k_BT_{\mathrm{rot}}j^2$ ($j = 0, 1, 2, \ldots$)*, where* $T_{\mathrm{rot}} = 150$ K. *The ground state of the rotator is non-*

*degenerate, whereas the degeneracy of all other states is* 2. *Calculate the change of entropy after a system consisting of* $10^{23}$ *independent rotators is heated from* 25 K *to* 30 K*! What is the result if the initial and the final temperature are* 1500 K *and* 1505 K, *respectively?*

The entropy can be calculated from $S = -\mathrm{d}F/\mathrm{d}T$ so that, as always, we first need to evaluate the partition function to obtain the Helmholtz free energy $F$. As with the three-dimensional rotator, the partition function cannot be calculated analytically, but we can estimate it at low and high temperatures.

At low temperatures, $T \ll T_{\mathrm{rot}}$, we spell out a few terms of the rapidly converging sum

$$\exp(-\beta F) \propto \left[1 + 2\exp\left(-\frac{T_{\mathrm{rot}}}{T}\right) + 2\exp\left(-4\frac{T_{\mathrm{rot}}}{T}\right) + \ldots\right]^N,$$

where $N$ is the number of independent rotators. In the temperature range considered here, it suffices to keep the first two terms in this sum and we find that

$$S = 2Nk_B\left(1 + \frac{T_{\mathrm{rot}}}{T}\right)\exp\left(-\frac{T_{\mathrm{rot}}}{T}\right).$$

The change of entropy upon heating from 25 K to 30 K is equal to 0.064 J/K.

On the other hand, at high temperatures where $T \gg T_{\mathrm{rot}}$, many rotational energy levels are occupied and the sum in the partition function can be replaced by an integral:

$$\begin{aligned}\exp(-\beta F) &= \left[\sum_{j=0}^{\infty} 2\exp\big(-\beta k_B T_{\mathrm{rot}} j^2\big) - 1\right]^N \\ &\approx \left[2\int_0^{\infty} \exp\big(-\beta k_B T_{\mathrm{rot}} j^2\big)\mathrm{d}j\right]^N \\ &= \left(\pi\frac{T}{T_{\mathrm{rot}}}\right)^{N/2}.\end{aligned}$$

The change of entropy upon heating upon heating from 1500 K to 1505 K is calculated just like in the low-temperature limit and is equal to

$$\Delta S = S(T) - S(T') = \frac{Nk_B}{2}\ln\left(\frac{T}{T'}\right) = 2.3\ \mathrm{mJ/K}.$$

The last result can also be obtained by a shortcut: In the high-temperature limit, the rotators behave like classical systems. Thus one can apply the equipartition theorem to the single rotational degree of freedom of each rotator to find that the average energy is equal to $\langle E\rangle = Nk_BT/2$ so that the corresponding heat capacity reads $C = Nk_B/2$. At this point, we can resort to thermodynamics and obtain the change of entropy using $\Delta S = \int_{T'}^{T}(C/T)\mathrm{d}T$, thereby immediately reproducing the above result.

**Problem 11.10.**
*Calculate the magnetization of gadolinium sulfate octahydrate in a magnetic field of flux density of* $2\ \mathrm{T}$ *at* $4\ \mathrm{K}$ *and at* $40\ \mathrm{K}$*! The magnetic moment of the substance is due solely to the gadolinium ions; their spin is* $7/2$ *and the gyromagnetic ratio equals* $e_0/m$ *(*$m$ *denotes the mass of electron). The density of gadolinium sulfate octahydrate* $\mathrm{Gd_2(SO_4)_3 \cdot 8H_2O}$ *is equal to* $3010\ \mathrm{kg/m^3}$*; the kilomolar masses of gadolinium, sulfur, and oxygen are* $157,\ 32,$ *and* $16\ \mathrm{kg/kmol}$*, respectively.*

The magnetic dipole moment of an atom with an angular momentum $\hbar j$ and the projection of the angular momentum onto the direction of the external field $\hbar j_z$ is equal to $p_z = \gamma\hbar j_z$, where $\gamma = e_0/m$ is the gyromagnetic ratio. The coupling with an external magnetic field of flux density $B$ results in $2j+1$ equidistant levels of energies

$$E(j_z) = -\gamma\hbar j_z B\,,$$

where $j_z = -j, -j+1, \ldots j-1, j$. The partition function is a geometric series

$$\exp(-\beta F) = \sum_{j_z=-j}^{j} \exp(\beta\gamma\hbar j_z B) = \frac{\sinh\bigl(\beta\gamma\hbar B(j+1/2)\bigr)}{\sinh(\beta\gamma\hbar B/2)}\,.$$

The average magnetic dipole moment of the atom is proportional to average energy: $\langle p_z\rangle = -\langle E\rangle/B$. Thus

$$\langle p_z\rangle = \gamma\hbar\left[\left(j+\frac{1}{2}\right)\coth\left(\frac{(j+1/2)T_m}{T}\right) - \frac{1}{2}\coth\left(\frac{T_m}{2T}\right)\right];$$

here we introduced the characteristic temperature $T_m = \gamma\hbar B/k_B$ related to the energy difference of adjacent energy levels which is, in the present case, equal to 2.675 K. $\langle p_z\rangle$ depends on the reduced temperature $T/T_m$: At low temperatures we have

$$\langle p_z\rangle = \gamma\hbar\left[j + (2j+1)\exp\left(-\frac{(2j+1)T_m}{T}\right) - \exp\left(-\frac{T_m}{T}\right)\right],$$

whereas at high temperatures a Taylor expansion yields

$$\langle p_z\rangle = \frac{\gamma\hbar j(j+1)T_m}{3T}\,.$$

As the characteristic temperature $T_m$ is proportional to $B$, this result contains the Curie law so that the magnetic susceptibility $\chi \propto 1/T$ (Fig. 11.5). This characteristic temperature dependence of the susceptibility is also obtained in a gaseous dielectric material (Problem 9.1), which is not surprising because at high temperatures the energy difference of adjacent magnetic levels is negligible compared to $k_BT$ and the discreteness of the spectrum is unimportant.

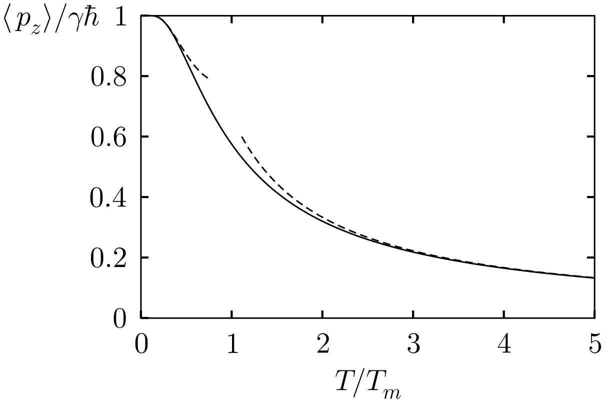

**Fig. 11.5** Average magnetic dipole moment of an atom of angular momentum $j = 1$ in a magnetic field as a function of reduced temperature (solid line) plotted together with the corresponding low- and high-temperature approximations (dashed lines)

Magnetization is the volumetric density of the magnetic dipole moment: $M = N\langle p_z\rangle/V$. The number density of the gadolinium ions is calculated from the density and kilomolar mass; note that each gadolinium sulfate molecule contains two gadolinium atoms. At 4 K the magnetization of $Gd_2(SO_4)_3 \cdot 8H_2O$ is $2.24 \times 10^5$ A/m, whereas at 40 K it is $3.15 \times 10^4$ A/m.

## Problem 11.11.

*Calculate the magnetic heat capacity of gadolinium sulfate octahydrate considered in Problem* 11.10 *in a field of* 2 T *at* 4 K *and* 40 K*!*

By differentiating the average energy derived in Problem 11.10, we find that the heat capacity of a single spin

$$C = k_B\left(\frac{T_m}{T}\right)^2\left[\frac{1}{4}\sinh^{-2}\left(\frac{T_m}{2T}\right) - \left(j+\frac{1}{2}\right)^2\sinh^{-2}\left(\frac{(j+1/2)T_m}{T}\right)\right].$$

It is easy to see that $C$ tends to 0 both at absolute zero and at very high temperatures, and hence we conclude that it must be a non-monotonic function of temperature. A more detailed analysis reveals that with increasing $j$, the height of the peak of the heat capacity approaches $k_B$ and the width of the peak increases (Fig. 11.6). Such behavior is understandable since by letting $j \to \infty$ we approach the classical limit; note that the magnetic energy is formally equivalent to the gravitational energy, which gives rise to a heat capacity of $k_B$ (see Problem 8.1).

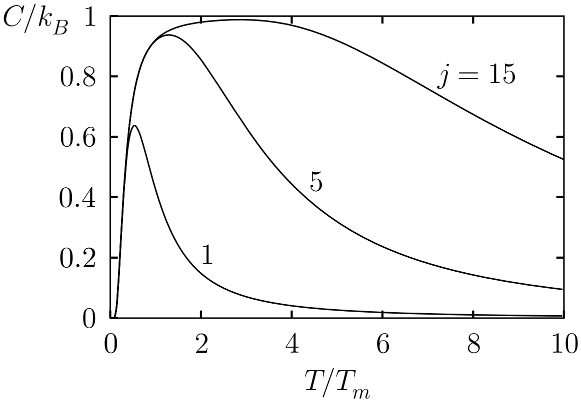

**Fig. 11.6** Magnetic heat capacity per atom as a function of reduced temperature, plotted for atoms with $j = 1, 5$, and 15. The higher the angular momentum, the higher and the broader the peak of $C(T)$

We also notice that the heat capacity of electric dipoles (Problem 9.2), treated within the framework of classical physics, is finite at low temperatures and does not drop to 0 like in magnetic dipoles. This qualitative difference originates in the discreteness of the energy levels which is a consequence of the quantum nature of the magnetic system: Upon heating, the internal energy of the system can only increase if the population of the first excited level is significant. Such a restriction is absent in systems with a continuous energy spectrum, e.g., in electric dipoles. On the other hand, the high-temperature limits of the classical and quantum system agree with each other. In both cases, one has $C \to 0$ because at $T \to \infty$ all states in phase space are equally populated.

The magnetic specific heat is now given by $c_H = 2N_AC/M$, where the factor of 2 accounts for the two gadolinium atoms in each molecule of gadolinium sulfate and $M = 746$ kg/kmol is the kilomolar mass of gadolinium sulfate octahydrate. In a magnetic field of 2 T, $c_H = 18.3$ J/kgK at 4 K and 0.51 J/kgK at 40 K.

## Problem 11.12.

*In the Ising model of a ferromagnet the interaction between atomic magnetic moments is described by the Hamiltonian*

$$H = -J \sum_{i,j \text{ neighbors}} s_i s_j ,$$

*where $J$ denotes the exchange integral and $s_i = \pm 1/2$. Calculate the temperature of the ferromagnetic–paramagnetic transition by using the mean-field approximation! The coordination number of the atoms is equal to $z$.*

In the mean-field approximation, the Ising Hamiltonian is replaced by

$$H = -\gamma\hbar \sum_i s_i \langle B\rangle\,,$$

where $\langle B\rangle$ is the magnetic flux density created by the neighboring atoms at the site of atom $i$. From the comparison of the interaction energies involving the spin at site $i$ in the original and in the substitute Hamiltonian we find that

$$\langle B\rangle = \frac{J}{\gamma\hbar}\sum_{j=1}^{z}\langle s_j\rangle = \frac{zJ}{\gamma\hbar}\langle s\rangle = \frac{zJ}{4p_B^2}\langle p_z\rangle\,,$$

where $z$ is the coordination number and $p_B = e_0\hbar/2m$ is the Bohr magneton. Now we take the expression for the average magnetic dipole moment of an isolated atom in an external magnetic field, which for atoms with angular momentum $1/2$ simplifies to $\langle p_z\rangle = p_B \tanh\left(p_B B/k_B T\right)$ (Problem 11.10), and we replace $B$ with the mean field $\langle B\rangle$. This leads to the equation of state

$$\frac{\langle p_z\rangle}{p_B} = \tanh\left(\frac{zJ}{4k_BT}\frac{\langle p_z\rangle}{p_B}\right)$$

or

$$\mathcal{M} = \tanh\frac{\mathcal{M}}{\mathcal{T}}\,,$$

where $\mathcal{M} = \langle p_z\rangle/p_B$ is the reduced magnetization and $\mathcal{T} = 4k_BT/zJ$ is the reduced temperature.

Close to phase transition which is at $\mathcal{T} = 1$, the equilibrium spontaneous magnetization is small and can be calculated by expanding $\tanh(\mathcal{M}/\mathcal{T})$ in a series. This yields

$$\mathcal{M} = \frac{\mathcal{M}}{\mathcal{T}} - \frac{\mathcal{M}^3}{3\mathcal{T}^3} + \ldots$$

with solutions $\mathcal{M} = 0$ (paramagnetic phase) and $\mathcal{M} = \pm\sqrt{3\mathcal{T}^2(1-\mathcal{T})}$ (ferromagnetic phase); the nontrivial solutions exist only for $\mathcal{T} < 1$. Close to the phase transition, the temperature dependence of the magnetization in the ferromagnetic phase differs from the spontaneous polarization in a ferroelectric material obtained within the local-field approximation (Problem 9.4) only by a numerical factor; the corresponding critical exponents are equal. At low temperatures where the reduced magnetization barely differs from 1, we have $\mathcal{M}(\mathcal{T}) \approx 1 - 2\exp\left(-2/\mathcal{T}\right)$. This approximation agrees with the exact numerical solution rather well, as does that obtained close to the transition (Fig. 11.7).

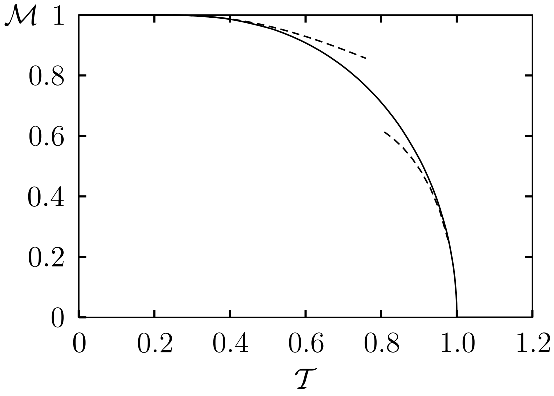

**Fig. 11.7** Ising model of the ferromagnetic–paramagnetic transition in the mean-field approximation: Exact temperature dependence of the reduced spontaneous magnetization (solid line) shown together with the approximations valid at low temperatures and close to the transition (dashed lines)

By recalling that the two spin states are separated by an energy gap of width $2p_B\langle B\rangle$, it is easy to understand why the temperature dependence of the spontaneous magnetization of the ferromagnetic phase is so weak close to absolute zero. On the other hand, the energy of an electric dipole in the ferroelectric phase (Problem 9.4) is not quantized, which leads to a more pronounced temperature dependence of the spontaneous electric polarization in the model ferroelectric material at low temperatures.

We finally note that in the mean-field approximation, there is no qualitative difference between one-, two-, and three-dimensional systems; the only parameter that changes is the coordination number. However, Problem 10.11 demonstrates that in the Ising model, the dimensionality of the system actually plays a key role in the very existence of a phase transition. We conclude that the concept of the mean-field concept is of limited applicability.

## Problem 11.13.

*By considering the mean-field approximation of the Ising model, explore the behavior of the heat capacity close to the ferromagnetic–paramagnetic transition!*

We assume that the magnetic field created at the site of the reference atom by the neighboring atoms $\langle B\rangle$ is weak enough so that we can estimate the average magnetic dipole moment of the reference atom using the high-temperature approximation (Problem 11.10). For $j = 1/2$ and $\gamma = e_0/m$, the average magnetic moment reads

$$\langle p_z\rangle = \frac{p_B^2\langle B\rangle}{k_BT}\,.$$

Here $p_B = e_0\hbar/2m$ is the Bohr magneton. The average energy of this magnetic moment is

$$\langle E\rangle = -\frac{1}{2}\langle p_z\rangle\langle B\rangle = -\frac{p_B^2\langle B\rangle^2}{2k_BT},$$

where the factor 1/2 is due to the pairwise nature of the interactions. Problem 11.12 shows that $\langle B\rangle = (zJ/4p_B)\mathcal{M}$, where $\mathcal{M}$ is the reduced spontaneous magnetization. Just below the phase transition at reduced temperature $\mathcal{T} = 1$ we have $\mathcal{M} \approx \sqrt{3\mathcal{T}^2(1-\mathcal{T})}$, whereas above the transition $\mathcal{M} = 0$. This gives

$$\langle E\rangle = \begin{cases} -3k_BT_c\mathcal{T}(1-\mathcal{T})/2, & \mathcal{T} < 1 \\ 0, & \mathcal{T} > 1 \end{cases};$$

$T_c = zJ/4k_B$ is the critical temperature. In the ferromagnetic phase close to $\mathcal{T} = 1$ the magnetic heat capacity of an atom increases linearly with temperature, whereas in the paramagnetic phase it is 0:

$$C = \begin{cases} 3k_B(\mathcal{T} - 1/2), & \mathcal{T} < 1 \\ 0, & \mathcal{T} > 1 \end{cases}.$$

Hence, the jump of the heat capacity at the transition equals $3k_B/2$ per atom. It is not surprising that a similar behavior is seen at the ferroelectric–paraelectric transition (Problem 9.6).

**Problem 11.14.**
*Calculate the heat capacity of a one-dimensional Ising model with periodic boundary conditions! Use the transfer matrix approach!*

The partition function

$$\exp(-\beta F) = \sum_{\{s_i\}} \exp\left(\beta J \sum_{i=1}^{N} s_i s_{i+1}\right),$$

where $\{s_i\}$ denotes the spin configuration of the entire system, contains terms of the form $\exp(\beta J s_1 s_2)\exp(\beta J s_2 s_3)\ldots\exp(\beta J s_N s_1)$. If we assign a spinor $|s_i\rangle = \begin{bmatrix}1\\0\end{bmatrix}$ to spin $s_i = +1/2$ and a spinor $|s_i\rangle = \begin{bmatrix}0\\1\end{bmatrix}$ to spin $s_i = -1/2$, each of the factors $\exp(\beta J s_i s_{i+1})$ can be regarded as a matrix element $\langle s_i|\mathsf{P}|s_{i+1}\rangle$, where

$$\mathsf{P} = \begin{bmatrix} \exp(\beta J/4) & \exp(-\beta J/4) \\ \exp(-\beta J/4) & \exp(\beta J/4) \end{bmatrix}.$$

The partition function can then be rewritten as

$$\exp(-\beta F) = \sum_{s_1=\pm 1/2}\sum_{s_2=\pm 1/2}\ldots\sum_{s_N=\pm 1/2} \langle s_1|\mathsf{P}|s_2\rangle\langle s_2|\mathsf{P}|s_3\rangle\ldots\langle s_N|\mathsf{P}|s_1\rangle.$$

Since the states $|s_i\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$ and $|s_i\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$ span a complete system, we have $\sum_{s_i} |s_i\rangle\langle s_i| = 1$ and hence

$$\exp(-\beta F) = \sum_{s_1=\pm 1/2} \langle s_1|\mathsf{P}^N|s_1\rangle = \operatorname{tr} \mathsf{P}^N.$$

The trace of the $\mathsf{P}^N$ matrix is easy to calculate if $\mathsf{P}^N$ is diagonalized first; we find that the eigenvalues of $\mathsf{P}$ are $2\cosh(\beta J/4)$ and $2\sinh(\beta J/4)$. Since $\cosh(\beta J/4) > \sinh(\beta J/4)$ for any value of $\beta J$, in the thermodynamic limit $N \to \infty$ we obtain

$$\exp(-\beta F) = \left[2\cosh\left(\frac{\beta J}{4}\right)\right]^N,$$

which formally coincides with the partition function for $N$ independent atoms with $j = 1/2$ in an external magnetic field (Problem 11.10) if $J$ is mapped into $2\gamma\hbar B$. As isolated magnetic moments in an external field are known not to give rise to a ferromagnetic phase, we conclude that no spontaneous order is predicted by the one-dimensional Ising model either. As shown in Problem 10.11, such order can occur only at absolute zero.

In agreement with Problems 11.10 and 11.11 the average energy of a one-dimensional Ising model is equal to $\langle E\rangle = -(NJ/4)\tanh(J/4k_BT)$ and the corresponding heat capacity reads

$$C = Nk_B\left(\frac{J}{4k_BT}\right)^2 \cosh^{-2}\left(\frac{J}{4k_BT}\right).$$

**Problem 11.15.**
*Discuss the conformational part of the partition function of a very long polyethylene chain! Calculate the average conformational energy per bond at* 300 K, *given that the energy of the trans state is lower than the energy of both gauche states by* 0.025 eV*! Explore the high- and the low-temperature behavior of the average energy!*

The nature of the conformations *trans* ($t$), *gauche*+ ($g^+$), and *gauche*− ($g^-$) in an alkane chain is discussed in Problem 8.12, where a short pentane chain is considered. Here, we turn to a non-branched long chain consisting of $N+1$ carbon atoms containing $N$ bonds, with $N-2$ neighboring-atom quartets. The state of the $i$-th quartet is denoted by $\varphi_i$, and the energy difference between the *gauche* and the *trans* state is $w$. Recall that the bonding sequences $g^+g^-$ and $g^-g^+$ for the neighboring quartets are prohibited and are thus assigned an infinite energy. The Hamiltonian of such a chain reads

$$H = \sum_{i=2}^{N-1} H_L(\varphi_i) + \sum_{i=3}^{N-1} H_N(\varphi_{i-1}, \varphi_i),$$

where the local term

$$H_L(\varphi_i) = \begin{cases} 0, & \varphi_i = t \\ w, & \varphi_i = g^\pm \end{cases}$$

represents the conformational energy of a given quartet, whereas the nonlocal term

$$H_N(\varphi_{i-1}, \varphi_i) = \begin{cases} \infty, & \{\varphi_{i-1}, \varphi_i\} = \{g^\pm, g^\mp\} \\ 0, & \{\varphi_{i-1}, \varphi_i\} \neq \{g^\pm, g^\mp\} \end{cases}$$

ensures that the $\{g^\pm, g^\mp\}$ bonding sequences do not appear in neighboring quartets. (The adjective "non-local" refers to the fact that unlike the $H_L$ term, the $H_N$ term depends on the states of two neighboring quartets.) $H$ is now recast as

$$H = H_L(\varphi_2) + \sum_{i=3}^{N-1} H_P(\varphi_{i-1}, \varphi_i)$$

with $H_P(\varphi_{i-1}, \varphi_i) = H_L(\varphi_i) + H_N(\varphi_{i-1}, \varphi_i)$. We notice that the Hamiltonian is similar to that of the Ising model in Problem 11.14 except that it features quartets instead of spins and that the quartets can be in one of the three possible states. Hence the partition function reads

$$\exp(-\beta F) = \sum_{\varphi_2} \dots \sum_{\varphi_{N-1}} \exp\big(-\beta H_L(\varphi_2)\big) \times \prod_{i=3}^{N-1} \exp\big(-\beta H_P(\varphi_{i-1}, \varphi_i)\big) .$$

Like in the transfer matrix approach of Problem 11.14, the states $\varphi_i$ can be represented by

$$|t\rangle = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}, \quad |g^+\rangle = \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}, \quad \text{and} \quad |g^-\rangle = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} .$$

Now the factors $\exp\big(-\beta H_P(\varphi_{i-1}, \varphi_i)\big)$ can be regarded as matrix elements $\langle \varphi_{i-1} | \mathsf{P} | \varphi_i \rangle$ where

$$\mathsf{P} = \begin{bmatrix} 1 & u & u \\ 1 & u & 0 \\ 1 & 0 & u \end{bmatrix}$$

with $u = \exp(-\beta w)$, and the partition function can be rewritten as

$$\exp(-\beta F) = \sum_{\varphi_2} \dots \sum_{\varphi_{N-1}} \exp\big(-\beta H_L(\varphi_2)\big) \times \langle \varphi_2 | \mathsf{P} | \varphi_3 \rangle \dots \langle \varphi_{N-2} | \mathsf{P} | \varphi_{N-1} \rangle .$$

[We note that unlike in Problem 11.14, $\mathsf{P}$ is not symmetric which is due to the presence of the local term $H_L(\varphi_i)$. In the Ising spin chain, such a term would appear if the chain were exposed to an external magnetic field, which would break the symmetry of the spin states.] The states $|t\rangle$, $|g^+\rangle$ in $|g^-\rangle$ span a complete system; therefore $\sum_{\varphi_i} |\varphi_i\rangle\langle\varphi_i| = 1$, and thus

$$\exp(-\beta F) = \sum_{\varphi_2}\sum_{\varphi_{N-1}} \exp\big(-\beta H_L(\varphi_2)\big)\,\langle\varphi_2|\mathsf{P}^{N-3}|\varphi_{N-1}\rangle\,.$$

The evaluation of the sums over the terminal quartets $|\varphi_2\rangle$ and $|\varphi_{N-1}\rangle$ can be avoided by assuming that there exists an additional carbon atom at either end of the chain and by requiring that the thus introduced additional quartets are both in the *trans* state; this is just a mathematical device. This does not increase the phase space and does not alter the partition function either (recall that the conformational energy of the *trans* states is zero). Thus the partition function is recast as

$$\exp(-\beta F) = \langle t|\mathsf{P}^{N-1}|t\rangle\,.$$

To facilitate the evaluation of the matrix $\mathsf{P}^{N-1}$, we first diagonalize it. We have $\mathsf{P} = \mathsf{A}\mathsf{D}\mathsf{A}^{-1}$, where $\mathsf{D}$ is a diagonal matrix with eigenvalues $\lambda_1$, $\lambda_2$, and $\lambda_3$, whereas $\mathsf{A}$ is the transition matrix. Furthermore, $\mathsf{P}^{N-1} = (\mathsf{A}\mathsf{D}\mathsf{A}^{-1})^{N-1} = \mathsf{A}\mathsf{D}^{N-1}\mathsf{A}^{-1}$ and

$$\mathsf{D}^{N-1} = \begin{bmatrix} \lambda_1^{N-1} & 0 & 0 \\ 0 & \lambda_2^{N-1} & 0 \\ 0 & 0 & \lambda_3^{N-1} \end{bmatrix},$$

yielding

$$\exp(-\beta F) = A_{11}A_{11}^{-1}\lambda_1^{N-1} + A_{12}A_{21}^{-1}\lambda_2^{N-1} + A_{13}A_{31}^{-1}\lambda_3^{N-1}\,.$$

[Here $A_{ij}^{-1}$ denotes $(\mathsf{A}^{-1})_{ij}$ rather than $1/A_{ij}$.] Assume now that $\lambda_1 > \lambda_2, \lambda_3$. In this case, the last two terms can be neglected in a long chain with $N \gg 1$, and after approximating $N-1$ by $N$ we are left with $\exp(-\beta F) \approx A_{11}A_{11}^{-1}\lambda_1^N$. Now we need to find the eigenvalues of the matrix $\mathsf{P}$. By requiring that $\det(\mathsf{P} - \lambda\mathsf{I}) = 0$ and solving the ensuing cubic equation for $\lambda$, we obtain $\lambda_{1,2} = [1 + u \pm \sqrt{(1+u)^2 + 4u}]/2$ and $\lambda_3 = u$. Finally, the Helmholtz free energy of the chain is given by $F = -k_BT[\ln(A_{11}A_{11}^{-1}) + N\ln\lambda_1(\beta)]$ where

$$\lambda_1(\beta) = \frac{1}{2}\left\{1 + \exp(-\beta w) + \sqrt{[1 + \exp(-\beta w)]^2 + 4\exp(-\beta w)}\right\}.$$

The average conformational energy per bond is equal to

$$\begin{aligned}\frac{\langle E\rangle}{N} &= \frac{1}{N}\frac{\mathrm{d}\beta F}{\mathrm{d}\beta} = -\frac{1}{\lambda_1(\beta)}\frac{\mathrm{d}\lambda_1(\beta)}{\mathrm{d}\beta}\\ &= wu\frac{1+(3+u)\left[(1+u)^2+4u\right]^{-1/2}}{1+u+[(1+u)^2+4u]^{1/2}}\,,\end{aligned}$$

which amounts to $0.33\,w \approx 8.3$ meV at 300 K.

In the end, we explore the low- and high-temperature behavior of the chain. At very low temperatures we obtain $\langle E\rangle/N \approx 2w\exp(-w/k_BT)$: Most of the quartets are in the *trans* state with zero energy, and the first excited state has an energy of $w$ and a degeneracy of 2. On the other hand, at high temperatures we have $\langle E\rangle/N \to w/2$. One may naively expect that $\langle E\rangle/N \to 2w/3$, since each of the quartets can be in any of the three different states which should be equally populated at high temperatures. However, we must not forget that two consecutive quartet bonding sequences ($g^+g^-$ and $g^-g^+$) are not allowed. The complete temperature dependence of $\langle E\rangle/N$ is plotted in Fig. 11.8.

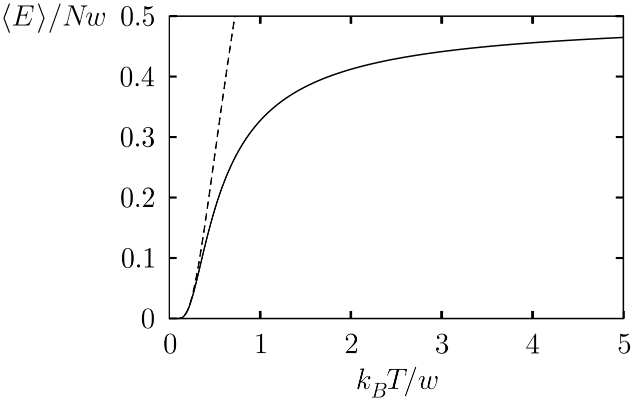

**Fig. 11.8** Average conformational energy originating from bonds between the carbon atoms in a polyethylene chain (solid line), together with its low-temperature approximation $\langle E\rangle/Nw \approx 2\exp(-w/k_BT)$ (dashed line)

### Problem 11.16.

*Analyze the ferromagnetic–paramagnetic transition in the one-dimensional Ising model with periodic boundary conditions using the renormalization group approach!*

We consider $2^N$ spins $s_1, s_2, \ldots s_{2^N}$ which can take values $\pm 1/2$. The periodic boundary conditions require that the spin $s_{2^N}$ is the left neighbor of the spin $s_1$. The partition function is equal to

$$\exp\bigl(-\beta F_N(J_N)\bigr) = \sum_{\{s_i\}}\exp\left(\beta J_N\sum_{i=1}^{2^N} s_i s_{i+1}\right),$$

where $\{s_i\}$ denotes a summation over all spin configurations. Here all spin–spin interactions are included only once; we emphasize that the partition function depends on the exchange integral $J_N$. Now we evaluate the contribution of spin $s_2$ to the partition function. This spin appears in two terms of the Hamiltonian: $J_N(s_1 s_2 + s_2 s_3) = J(s_1 + s_3)s_2$. We obtain

$$\exp\bigl(-\beta F_N(J_N)\bigr) = \sum_{\{s_i,\overline{s_2}\}} \exp\Bigl(\beta J_N \sum_{i=3}^{2^N} s_i s_{i+1}\Bigr) \times \underbrace{\sum_{s_2=\pm 1/2} \exp\bigl(\beta J_N (s_1+s_3)s_2\bigr)}_{2\cosh\left(\beta J_N(s_1+s_3)/2\right)} .$$

If the contribution of spin $s_2$ to the partition function is written as

$$2\cosh\left(\frac{\beta J_N(s_1+s_3)}{2}\right) = \begin{cases} 2\cosh\left(\beta J_N/2\right), & s_1 s_3 = +1/4 \\ 2, & s_1 s_3 = -1/4 \end{cases} ,$$

we see that it only depends on the product of spins $s_1$ and $s_3$ and that it can be regarded as a term in the Ising Hamiltonian that couples spins $s_1$ and $s_3$:

$$2\cosh\left(\frac{\beta J_N(s_1+s_3)}{2}\right) = D_{N-1}\exp\left(\beta J_{N-1} s_1 s_3\right) .$$

Here $D_{N-1} = 2\sqrt{\cosh\left(\beta J_N/2\right)}$ is a factor added to the normalization constant of the partition function, and

$$J_{N-1} = \frac{4}{\beta}\ln\sqrt{\cosh\left(\frac{\beta J_N}{2}\right)}$$

is the effective exchange integral between spins $s_1$ and $s_3$. Now we use the same procedure for all remaining even-labeled spins to find that

$$\exp\bigl(-\beta F_N(J_N)\bigr) = D_{N-1}^{2^{N-1}}\exp\bigl(-\beta F_{N-1}(J_{N-1})\bigr) .$$

In this manner, we transformed the sum over all configurations of the initial $2^N$ spins into a sum over $2^{N-1}$ odd-labeled spins, with the spin–spin exchange integral of $J_{N-1}$ instead of $J_N$. This spin decimation procedure can be repeated to remove spins $s_3$, $s_7$, $s_{11}$, … from the partition function so as to obtain the effective exchange integral between spins $s_1$ and $s_5$, $s_5$ and $s_9$, …, which evidently obeys the relation $J_{N-2} = (4/\beta)\ln\sqrt{\cosh(\beta J_{N-1}/2)}$ (Fig. 11.9).

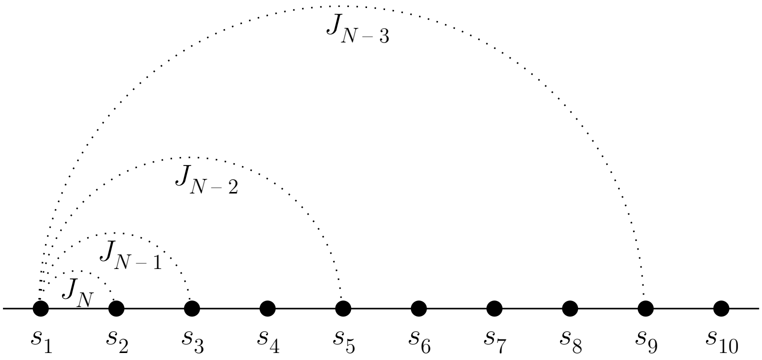

**Fig. 11.9** Decimation of spins on a one-dimensional lattice. The original exchange integral between neighboring spins is $J_N$, the effective exchange integral between next-nearest neighbors is $J_{N-1}$, that between next-next-nearest neighbors is $J_{N-2}$...At the critical point, the exchange integrals between a given spin and any other spin in the chain must be the same

Since the phase transition from the ferromagnetic to the paramagnetic phase is continuous, it is accompanied by strong fluctuations without a characteristic correlation length. This means that at transition temperature, the exchange integral between any two spins in the system is equally strong. In other words, the phase transition corresponds to the fixed point in the recursive scheme $J_N \to J_{N-1} \to J_{N-2} \to \dots$ By rewriting the relation between $J_{N-1}$ and $J_N$ as $\exp(\beta J_{N-1}/4) = \sqrt{\cosh(\beta J_N/2)}$ or

$$\exp\left(\frac{\beta J_{N-1}}{2}\right) = \frac{1}{2}\left[\exp\left(\frac{\beta J_N}{2}\right) + \exp\left(-\frac{\beta J_N}{2}\right)\right] < \exp\left(\frac{\beta J_N}{2}\right),$$

we see that $J_{N-1} < J_N$ so that the effective exchange integral decreases with each step of the iteration. This is equivalent to saying that in each step, the characteristic temperature associated with the effective exchange integral increases (Fig. 11.10).

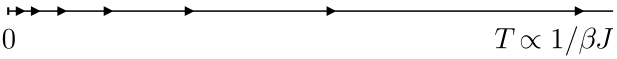

**Fig. 11.10** Renormalization group flow: In each decimation step, the effective exchange integral is decreased, which can be interpreted as an increase of the effective temperature. The fixed points are $T = 0$ (repulsive) and $T \to \infty$ (attractive)

Now we look for the critical point where one has $J_i = J_{i-1} = J^*$, or

$$\beta J^* = 2 \ln \cosh\left(\frac{\beta J^*}{2}\right).$$

This equation has two solutions: The first one is $\beta J^* = 0$, which corresponds to the phase transition at $T \to \infty$ and thus disagrees with the usual notion of a critical point, whereas the second one is $\beta J^* = \infty$ or $T = 0$. This solution tells us that in our system the ferromagnetic–paramagnetic transition phase takes place at absolute zero. Consequently, there exists no ferromagnetic order in one dimension at any $T > 0$, which agrees with the results of Problem 10.11 as well as with the van Hove theorem mentioned in Problem 9.19.

**Problem 11.17.**

*The interaction between nearest-neighbor spins in a linear chain consisting of N spins is modeled by the Ising Hamiltonian*

$$H = -J \sum_{i=1}^{N-1} s_i s_{i+1},$$

*where $J$ is the exchange integral and $s_i = \pm 1/2$. Calculate the average value of $\langle s_1 s_N \rangle$ for $N = 3$ and $N = 12$, assuming $J/k_BT = 4$!*

The quantity $\langle s_1 s_N \rangle$ can be used to quantify the correlations of spin orientation along the chain. For $N = 3$, all $2^3 = 8$ microstates of the spin chain can be listed explicitly, and $\langle s_1 s_3 \rangle$ can then be calculated using the definition of a thermal average. For $N = 12$ (and any arbitrarily large $N$), this approach fails because the phase space consisting of $2^N$ microstates is too large. Instead we can write

$$\langle s_1 s_N \rangle = \frac{1}{4} P_+ + \left(-\frac{1}{4}\right) P_- ,$$

where $P_+$ and $P_-$ denote the probabilities that the terminal spins $s_1$ and $s_N$ be parallel or antiparallel, respectively. The probability that two neighboring spins are antiparallel is given by

$$p = \frac{\exp(-\beta J/4)}{\exp(-\beta J/4) + \exp(\beta J/4)} ;$$

the probability that they are parallel is $1 - p$. The terminal spins are thus parallel only if the chain contains an even number ($k$) of antiparallel spin pairs in the chain (and, inevitably, $N - k - 1$ parallel spin pairs). The corresponding probability is given by

$$P_+ = \sum_{k \text{ even}} \frac{(N-1)!}{k!(N-k-1)!} p^k (1-p)^{N-k-1}.$$

Analogously, an odd number of antiparallel neigboring pairs yields antiparallel terminal spins, and the expression for the corresponding probability $P_-$ differs from $P_+$ only in the sum running over odd rather than even values of $k$. By combining the above expressions and using the binomial theorem we obtain

$$\langle s_1 s_N \rangle = \frac{1}{4} \sum_{k=1}^{N} \frac{(N-1)!}{k!(N-k-1)!} p^k (1-p)^{N-k-1} (-1)^k = \frac{1}{4} (1-2p)^{N-1}$$

and upon inserting the result for $p$ we finally find

$$\langle s_1 s_N \rangle = \frac{1}{4}\left[\tanh\left(\frac{\beta J}{4}\right)\right]^{N-1}.$$

For $N = 3$ we have $\langle s_1 s_3 \rangle = 0.145$ whereas for $N = 12$, $\langle s_1 s_{12} \rangle = 0.0125$. We see that the correlations of spin orientation weaken with increasing spin-to-spin distance since $|\tanh(\beta J/4)| < 1$.

The same approach can be used to study directional correlations in a linear polymer chain where the angle between the consecutive monomers can be either 0 or $\pi$, the latter carrying an excess energy of $\phi_0$. Let the unit vector $\mathbf{u}_i$ point from the tail to the head of the $i$-th monomer. Using the reasoning developed for the Ising chain, the average $\langle \mathbf{u}_1 \cdot \mathbf{u}_k \rangle$ is equal to $(1-2p)^{k-1}$ where $p = 1/[1+\exp(\beta\phi_0)]$ is the probability that a given bond is bent; note that $p \leq 1/2$. The above result can be used to calculate, e.g., the persistence length of the polymer (defined in Problem 8.10)

$$\begin{aligned}\ell_p &= a \lim_{N\to\infty} \sum_{k=1}^{N} \langle \mathbf{u}_1 \cdot \mathbf{u}_k \rangle = a \lim_{N\to\infty} \frac{1-(1-2p)^N}{2p} \\ &= \frac{a}{2p} = \frac{a}{2}\left[1+\exp(\beta\phi_0)\right],\end{aligned}$$

where $a$ is the monomer length. Limiting cases: For $\beta\phi_0 \to \infty$ (low temperatures or a very stiff polymer) $\ell_p$ diverges, whereas for $\beta\phi_0 \to 0$ (high temperatures or a very flexible polymer) the orientational correlations between the monomers vanish and $\ell_p \to a$.

# Chapter 12
# Grand Canonical Ensemble

**Problem 12.1.**
*Examine the temperature dependence of the spin-wave (magnon) heat capacity in a ferromagnet close to absolute zero! The dispersion relation for magnons reads* $\omega = aq^2$.

The elementary excitations in a ferromagnet can be viewed as a system of independent harmonic oscillators. The number of excitation quanta is not conserved since they are virtual rather than real particles; consequently, their chemical potential is 0. In this case the occupation number of a given oscillator is equal to $\left[\exp\left(\hbar\omega/k_BT\right) - 1\right]^{-1}$. Within the Debye model, the average energy of excitations reads

$$\langle E\rangle = \int_0^{\omega_{\max}} \left[\frac{1}{\exp\left(\hbar\omega/k_BT\right) - 1} + \frac{1}{2}\right] \hbar\omega \, \mathrm{d}N(\omega)\,.$$

(Note that the term $\hbar\omega/2$ in the integrand representing the zero-point energy can well be omitted as it does not contribute to heat capacity.) The analysis can be easily generalized to a dispersion relation of the form $\omega = aq^n$ so as to apply to other kinds of excitations. The number of oscillators in the frequency interval between $\omega - \mathrm{d}\omega/2$ and $\omega + \mathrm{d}\omega/2$ for a single polarization of waves is given by

$$\mathrm{d}N(\omega) = \frac{V}{(2\pi)^3} 4\pi q^2 \mathrm{d}q = \frac{V}{2\pi^2 na}\left(\frac{\omega}{a}\right)^{3/n-1} \mathrm{d}\omega\,,$$

so that the heat capacity becomes

$$\begin{aligned} C = \frac{\mathrm{d}\langle E\rangle}{\mathrm{d}T} &= \frac{V\hbar^2}{2\pi^2 nk_BT^2a^{3/n}} \int_0^{\omega_{\max}} \frac{\omega^{3/n+1}\exp\left(\hbar\omega/k_BT\right)\,\mathrm{d}\omega}{\left[\exp\left(\hbar\omega/k_BT\right) - 1\right]^2} \\ &= k_B\frac{V}{2\pi^2 n}\left(\frac{k_BT}{\hbar a}\right)^{3/n} \int_0^{u_{\max}} \frac{u^{3/n+1}\exp u\,\mathrm{d}u}{(\exp u - 1)^2}\,, \end{aligned}$$

G. Skačej and P. Ziherl, *Solved Problems in Thermodynamics and Statistical Physics*, https://doi.org/10.1007/978-3-030-27661-4_12

with $u = \hbar\omega/k_BT$. In the Debye model, the upper bound of the integral is determined by the requirement that the total number of oscillators be equal to the number of single-particle degrees of freedom which is proportional to the number of atoms in the system. At low temperatures, however, this requirement is inessential because the integral converges rapidly and only weakly depends on the upper bound $u_{\max} \gg 1$. As a result, the temperature dependence of the heat capacity originates in the prefactor $T^{3/n}$ which gives $c_V \propto T^{3/2}$ for magnons with $n = 2$, whereas for phonons (i.e., sound waves) with $n = 1$ we have $c_V \propto T^3$. Note that the exponent also depends on the dimensionality of the system: In two-dimensional systems one has $c_V \propto T^{2/n}$ and in one-dimensional ones $c_V \propto T^{1/n}$.

**Problem 12.2.**
*Explore the behavior of the heat capacity of a solid at high temperatures! Analyze its deviation from the Dulong–Petit high-temperature limit for iron at* 300 °C*! The kilomolar mass of iron is* 55.8 kg, *its density is* $7800\,\mathrm{kg/m^3}$, *and the Young's modulus is* $1.1 \times 10^{11}\ \mathrm{N/m^2}$.

We assume that all three polarizations of sound propagate at the same velocity denoted by $c$. According to Problem 12.1, the average energy of phonons in a solid is given by

$$\langle E\rangle = \frac{3V\hbar}{2\pi^2c^3}\int_0^{\omega_{\max}} \frac{\omega^3\,\mathrm{d}\omega}{\exp(\hbar\omega/k_BT)-1} = \frac{3V(k_BT)^4}{2\pi^2c^3\hbar^3}\int_0^{u_{\max}} \frac{u^3\,\mathrm{d}u}{\exp u - 1}\,,$$

where $u = \hbar\omega/k_BT$. The upper bound of the spectrum is determined by the condition

$$3N = \frac{3V}{2\pi^2c^3}\int_0^{\omega_{\max}} \omega^2\,\mathrm{d}\omega = \frac{V\omega_{\max}^3}{2\pi^2c^3}\,.$$

This gives $\omega_{\max} = 2\pi c\,(3N/4\pi V)^{1/3}$ and $u_{\max} = \hbar\omega_{\max}/k_BT = T_D/T$; here $T_D = \hbar\omega_{\max}/k_B$ is the Debye temperature. At high temperatures, one has $u_{\max} \ll 1$ and $\langle E\rangle$ can be calculated by expanding the integrand into a series:

$$\begin{aligned}\langle E\rangle &\approx \frac{9Nk_BT^4}{T_D^3}\int_0^{u_{\max}}\left(u^2 - \frac{u^3}{2} + \frac{u^4}{12} + \ldots\right)\mathrm{d}u \\ &= 3Nk_BT\left[1 - \frac{3}{8}\frac{T_D}{T} + \frac{1}{20}\left(\frac{T_D}{T}\right)^2 + \ldots\right].\end{aligned}$$

Thus the heat capacity of phonons is equal to

$$C = 3Nk_B\left[1 - \frac{1}{20}\left(\frac{T_D}{T}\right)^2 + \ldots\right]$$

which agrees with the exact value fairly well; at $T/T_D = 0.5$, e.g., the difference is about 3% (Fig. 12.1).

From the data for iron we find that $c = \sqrt{E/\rho} = 3755$ m/s and $T_D = 492$ K: At 300 °C the heat capacity is equal to 428.8 J/kgK, which is 3.7% less than the high-temperature limit of 445.2 J/kgK.

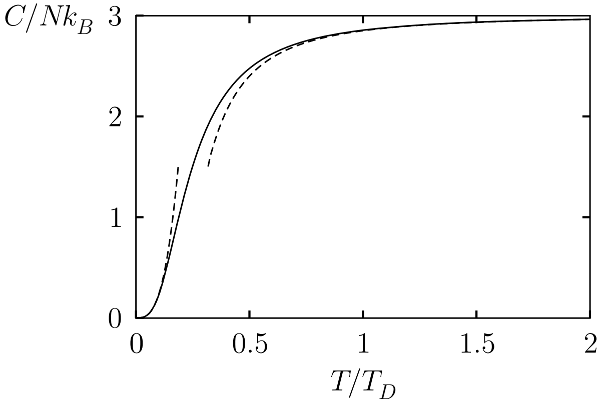

**Fig. 12.1** Heat capacity of a solid predicted by the Debye model (solid line), together with the low-temperature approximation $(12\pi^4 Nk_B/5)(T/T_D)^3$ and the high-temperature approximation $3Nk_B\left[1-(T_D/T)^2/20\right]$ (dashed lines)

### Problem 12.3.

*Up to what temperature must one heat a one-kilogram copper sample for the average number of phonons to double if its initial temperature is* 300 K*? Use the Einstein model of independent harmonic oscillators of frequency of* $4\times10^{13}$ s$^{-1}$*! Also calculate the change of the entropy of lattice vibrations upon heating! The kilomolar mass of copper is* 64 kg/kmol.

The energy of a single harmonic oscillator with $n$ phonons is $(n+1/2)\hbar\omega_E$, where $\omega_E$ is the oscillator frequency. The partition function of the oscillator is a geometric series:

$$\exp(-\beta F) = \sum_{n=0}^{\infty} \exp\left(-\beta\left(n+\frac{1}{2}\right)\hbar\omega_E\right) = \frac{\exp(-\beta\hbar\omega_E/2)}{1-\exp(-\beta\hbar\omega_E)}\,.$$

The average number of phonons in a given oscillator is

$$\langle n\rangle = \frac{\mathrm{d}\beta F}{\mathrm{d}\beta\hbar\omega_E} - \frac{1}{2} = \frac{1}{\exp(\beta\hbar\omega_E)-1}\,.$$

By requiring that $\langle n\rangle(T) = 2\langle n\rangle(T')$, i.e., that

$$\frac{1}{\exp(\beta\hbar\omega_E) - 1} = \frac{2}{\exp(\beta'\hbar\omega_E) - 1},$$

where $\beta' = 1/k_B T'$ and $T' = 300$ K, one concludes that the average phonon number is doubled at a temperature

$$T = \frac{\hbar\omega_E}{k_B}\left[\ln\left(\frac{\exp(\beta'\hbar\omega_E) + 1}{2}\right)\right]^{-1} = 482\ \mathrm{K}.$$

The entropy of lattice vibrations is equal to $S = \big(\langle E\rangle - F\big)/T$, where

$$\langle E\rangle = \frac{\mathrm{d}\beta F}{\mathrm{d}\beta} = \left(\langle n\rangle + \frac{1}{2}\right)\hbar\omega_E$$

is the average energy of a single oscillator. Finally we obtain

$$S(T) = k_B\left[\frac{\hbar\omega_E/k_B T}{\exp(\hbar\omega_E/k_B T) - 1} - \ln\left(1 - \exp\left(-\frac{\hbar\omega_E}{k_B T}\right)\right)\right].$$

This result applies to a single degree of freedom. In a crystal there are $3N$ degrees of freedom, where $N = mN_A/M$ is the total number of atoms, $m$ is the mass of the sample, and $M$ is the kilomolar mass of copper. The change of entropy of the one-kilogram copper sample upon heating from $T'$ to $T$ is then equal to

$$\frac{3mN_A}{M}\big[S(T) - S(T')\big] = 174\ \mathrm{J/K}.$$

**Problem 12.4.**
*A one-dimensional solid can be represented by a linear chain consisting of $N$ atoms, with nearest neighbors connected by springs. The eigenfrequencies of longitudinal waves propagating along such a chain are given by*

$$\omega_q = \omega_0\sqrt{2(1 - \cos qa)},$$

*with $q = 2\pi n/Na$, where $n$ is an integer between $-N/2$ and $N/2$, and $a = 1$ nm is the distance between nearest-neighbor atoms. What is the heat capacity of such a chain at high temperatures? Also examine its temperature dependence close to absolute zero and estimate its value at 1 K for $\omega_0 = 10^{12}\ \mathrm{s}^{-1}$!*

Since the number of atoms is rather large, the solid can be viewed as a continuum and $q$ can be treated as a continuous variable. The heat capacity of the chain is calculated from average energy

$$\begin{aligned}\langle E\rangle &= \int_0^{\omega(\pi/a)} \frac{\hbar\omega}{\exp(\beta\hbar\omega)-1}\, g(\omega)\,\mathrm{d}\omega \\ &= \int_{-\pi/a}^{\pi/a} \frac{\hbar\omega(q)}{\exp\big(\beta\hbar\omega(q)\big)-1}\,\frac{Na}{2\pi}\,\mathrm{d}q\,,\end{aligned}$$

where $g(\omega)$ denotes the density of states. We took into account that in one dimension, the number of independent harmonic oscillators in a wavevector interval $\mathrm{d}q$ is equal to $(Na/2\pi)\,\mathrm{d}q$ and that there exists only one polarization of the longitudinal waves.

At high temperatures we have $\exp(\beta\hbar\omega) \approx 1 + \beta\hbar\omega$ so that

$$\langle E\rangle = \int_0^{\pi/a} \frac{1}{\beta}\frac{Na}{\pi}\,\mathrm{d}q = Nk_BT\,.$$

Hence the specific heat is equal to $c_V = N^{-1}\,(\partial\langle E\rangle/\partial T)_V = k_B$, which completely agrees with the classical picture of lattice vibrations.

On the other hand, at low temperatures only the long-wave modes close to $q = 0$ are excited. For these states we can write $\cos(qa) \approx 1 - q^2a^2/2$, which yields an approximately linear dependence of $\omega(q)$: $\omega(q) \approx \omega_0|qa|$ (Fig. 12.2). We now obtain

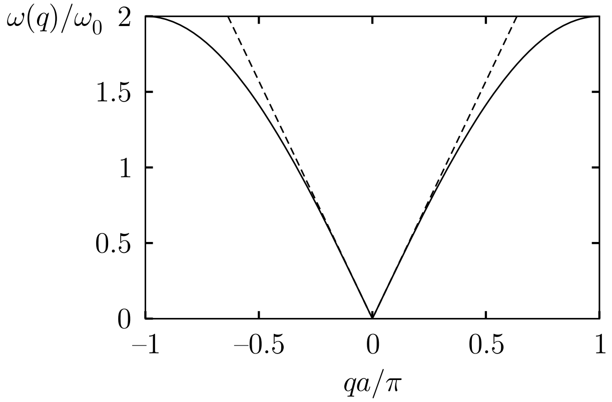

**Fig. 12.2** Dispersion relation for waves in a one-dimensional solid (solid line) and the linear dependence used to calculate the heat capacity at low temperatures (dashed line)

$$\langle E\rangle = \int_0^{\pi/a} \frac{\hbar\omega_0 qa}{\exp(\beta\hbar\omega_0 qa)-1}\,\frac{Na}{\pi}\,\mathrm{d}q = \frac{N}{\pi\hbar\omega_0\beta^2}\int_0^{\pi\beta\hbar\omega_0} \frac{u\,\mathrm{d}u}{\exp u - 1}\,.$$

At low temperatures, the upper bound of the integral can be pushed to infinity. From the tables of integrals we find that $\int_0^\infty [\exp u - 1]^{-1} u\, \mathrm{d}u = \pi^2/6$. Finally, at 1 K we have

$$c_V = \frac{\pi k_B^2 T}{3\hbar\omega_0} \approx 0.137\, k_B = 1.89 \times 10^{-24}\ \mathrm{J/K}\,.$$

At low temperatures, the heat capacity is a linear function of temperature, which agrees with the result of Problem 12.1.

**Problem 12.5.**

*The spectrum of elementary excitations in superfluid helium is rather peculiar: At wavevectors below* $0.8 \times 10^{10}/\mathrm{m}$, *the usual phonon dispersion relation* $E(q) = \hbar c q$ *applies, whereas for excitations with wavevectors around* $q_0 = 2 \times 10^{10}/\mathrm{m}$ *known as rotons one has*

$$E(q) = \Delta + \frac{\hbar^2}{2m}(q - q_0)^2\,,$$

*where* $\Delta = 0.746$ meV *and* $m = 1.2 \times 10^{-27}$ kg. *Calculate the roton heat capacity per unit volume in helium at* 2 K*!*

Like all elementary excitations, rotons too are bosons with zero chemical potential, and hence the corresponding grand potential $\Omega$ can be obtained from

$$\beta\Omega = \sum_j \ln\bigl(1 - \exp\left(-\beta E_j\right)\bigr) = \left(\frac{V}{2\pi^2}\right)\int_0^\infty \ln\bigl(1 - \exp\left(-\beta E\right)\bigr) q^2\, \mathrm{d}q\,,$$

with $E = E(q)$. Since at 2 K $\beta E \geq \beta\Delta \approx 4.3$, one can approximately put $\ln\bigl(1 - \exp(-\beta E)\bigr) \approx -\exp(-\beta E)$. The integral converges rapidly, and thus its lower bound can be safely extended from 0 to $-\infty$, which simplifies the calculation. After introducing a new variable $\widetilde{q} = q - q_0$

$$\begin{aligned}
\beta\Omega &\approx -\frac{V}{2\pi^2}\exp(-\beta\Delta)\int_{-\infty}^{\infty}\exp\left(-\frac{\beta\hbar^2}{2m}\widetilde{q}^2\right)(\widetilde{q} + q_0)^2\, \mathrm{d}\widetilde{q} \\
&= -\frac{V}{2\pi^2}\exp(-\beta\Delta)\sqrt{\frac{2\pi m}{\beta\hbar^2}}\left(\frac{m}{\beta\hbar^2} + q_0^2\right) \\
&\approx -\frac{V}{2\pi^2}\exp(-\beta\Delta)\sqrt{\frac{2\pi m}{\beta\hbar^2}}\, q_0^2\,,
\end{aligned}$$

where at the end we took into account that $m/\beta\hbar^2 q_0^2 = 7.5 \times 10^{-3} \ll 1$.

Thus the average energy of rotons is

$$\langle E\rangle = \frac{V q_0^2}{2\pi^2}\sqrt{\frac{2\pi m}{\hbar^2}}\left(\frac{1}{2} + \frac{\Delta}{k_B T}\right)(k_B T)^{3/2}\exp\left(-\frac{\Delta}{k_B T}\right)$$

and their heat capacity per unit volume

$$C/V = k_B \frac{q_0^2}{2\pi^2}\sqrt{\frac{2\pi m k_B T}{\hbar^2}}\left[\frac{3}{4} + \frac{\Delta}{k_B T} + \left(\frac{\Delta}{k_B T}\right)^2\right]\exp\left(-\frac{\Delta}{k_B T}\right);$$

in helium at 2 K, this amounts to $3.82 \times 10^5\ \mathrm{J/m^3K}$.

**Problem 12.6.**

*The dispersion relation of longitudinal waves in a one-dimensional solid is given by* $\omega(q) = \omega_0 + \alpha q^2$, *where* $\omega_0 = 10^{13}\ \mathrm{s}^{-1}$ *and* $\alpha = 30\ \mathrm{m^2/s}$. *How many optical phonons per unit length are there in the solid at low temperatures, say at* 10 K*? Calculate the phonon heat capacity of a meter-long sample!*

In one dimension, the sum over the allowed wave vectors is transformed into an integral: $\sum_j \to (L/\pi)\int \mathrm{d}q$, where $L$ denotes the length of the sample. Then the average number of phonons in the sample is given by

$$\langle N\rangle = \sum_j \frac{1}{\exp(\beta\hbar\omega_j) - 1} = \frac{L}{2\pi\sqrt{\alpha}}\int_{\omega_0}^{\omega_{\max}} \frac{\mathrm{d}\omega}{\left[\exp(\beta\hbar\omega) - 1\right]\sqrt{\omega - \omega_0}}.$$

By taking into account that even at the lowest $\omega$ we have $\exp(\beta\hbar\omega) \gg 1$ this result can be approximated by

$$\langle N\rangle = \frac{L}{2\pi\sqrt{\alpha\beta\hbar}}\exp(-\beta\hbar\omega_0)\int_0^{u_{\max}} \frac{\exp(-u)}{\sqrt{u}}\mathrm{d}u\,,$$

where we introduced $u = \beta\hbar(\omega - \omega_0)$. In the low-temperature limit one may set $u_{\max} \to \infty$ before evaluating the remaining integral; if we do so it reduces to $\Gamma(1/2) = \sqrt{\pi}$. Thus the density of phonons in the solid is

$$\frac{\langle N\rangle}{L} = \frac{\exp(-\beta\hbar\omega_0)}{2\sqrt{\alpha\beta\hbar\pi}} = 28\ \mathrm{m}^{-1}.$$

Similarly, the grand potential (needed for the evaluation of the internal energy and the heat capacity) is calculated as follows:

$$\beta\Omega = \sum_j \ln\left(1 - \exp(-\beta\hbar\omega_j)\right) = \frac{L}{2\pi\sqrt{\alpha}}\int_{\omega_0}^{\omega_{\max}} \frac{\ln\left(1 - \exp(-\beta\hbar\omega)\right)}{\sqrt{\omega - \omega_0}}$$

Again $\exp(-\beta\hbar\omega) \ll 1$ so that the logarithm can be expanded up to first order which eventually leads to the same dimensionless integral as in the above calculation of $\langle N\rangle$. Thus

$$\beta\Omega = -\frac{L\exp(-\beta\hbar\omega_0)}{2\sqrt{\alpha\beta\hbar\pi}}$$

and

$$\langle E\rangle = \left(\frac{\partial \beta\Omega}{\partial \beta}\right)_L = \frac{L\exp\left(-\beta\hbar\omega_0\right)}{2\sqrt{\alpha\beta\hbar\pi}}\left(\hbar\omega_0 + \frac{1}{2\beta}\right).$$

Finally,

$$C = \frac{\mathrm{d}\langle E\rangle}{\mathrm{d}T} = k_B\frac{L\exp\left(-\beta\hbar\omega_0\right)}{2\sqrt{\alpha\beta\hbar\pi}}\left[(\beta\hbar\omega_0)^2 + \beta\hbar\omega_0 + \frac{3}{4}\right] = 0.16\,\mathrm{eV/K}.$$

**Problem 12.7.**
*Calculate the pressure of blackbody radiation at* 300 K*! At this temperature, evaluate the entropy and the average number of photons within a cavity of a volume of* 1 cm$^3$*!*

The blackbody radiation too can be represented by a system of independent harmonic oscillators with frequencies given by $\omega_j = cq_j$, where $c$ is the speed of light in vacuum and $q_j$ are the corresponding wavevectors. The grand canonical partition function reads $\exp\left(-\beta\Omega\right) = \prod_j\left[1-\exp\left(-\hbar\omega_j/k_BT\right)\right]^{-1}$ because photons are bosons and because their chemical potential is equal to 0. From the relation $\Omega = -pV$, where $p$ is the pressure and $V$ is the volume, it follows that $pV = -k_BT\sum_j\ln\bigl(1-\exp(-\hbar\omega_j/k_BT)\bigr)$. By replacing the sum over all oscillators by an integral, $\sum_j \to (V/\pi^2)\int_0^\infty q^2\,\mathrm{d}q$ (recall that light has two independent polarizations), we further obtain

$$\begin{aligned}
pV &= -\frac{k_BTV}{\pi^2}\int_0^\infty \ln\left(1-\exp\left(-\frac{\hbar cq}{k_BT}\right)\right)q^2\,\mathrm{d}q\\
&= -\frac{V(k_BT)^4}{\pi^2(\hbar c)^3}\int_0^\infty \ln\bigl(1-\exp(-u)\bigr)u^2\,\mathrm{d}u\\
&= \frac{V(k_BT)^4}{\pi^2(\hbar c)^3}\sum_{n=1}^{\infty}\int_0^\infty \frac{\exp(-nu)u^2}{n}\,\mathrm{d}u\\
&= \frac{V(k_BT)^4}{\pi^2(\hbar c)^3}\sum_{n=1}^{\infty}\frac{2}{n^4} = \frac{\pi^2V(k_BT)^4}{45(\hbar c)^3}.
\end{aligned}$$

Here we introduced $u = \hbar cq/k_BT$ and we took into account that $\sum_{n=1}^{\infty}n^{-4} = \zeta(4) = \pi^4/90$; $\zeta(s)$ is the Riemann zeta function. From here we have

$$p = \frac{4\sigma}{3c}T^4,$$

where

$$\sigma = \frac{\pi^2k_B^4}{60\hbar^3c^2} = 5.67\times10^{-8}\ \mathrm{W/m^2K^4}$$

is the Stefan–Boltzmann constant. At 300 K, the pressure of light is equal to $2.04\times10^{-6}$ Pa. The fact that the number of photons is not constant is reflected in the pressure of light depending on temperature but not on volume, so that the isothermal compressibility of the photon gas is infinite.

The entropy is calculated by first realizing that in particles with zero chemical potential the Helmholtz free energy coincides with the grand potential so that $F = -pV = -4\sigma VT^4/3c$. Thus we have

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = \frac{16\sigma}{3c}VT^3 = 2.72 \times 10^{-14}\ \mathrm{J/K}\,.$$

Let us now evaluate the average number of photons inside the cavity:

$$\begin{aligned}\langle N\rangle &= \sum_j \frac{1}{\exp(\hbar\omega_j/k_BT) - 1} = \frac{V}{\pi^2}\left(\frac{k_BT}{\hbar c}\right)^3 \int_0^\infty \frac{u^2\,\mathrm{d}u}{\exp u - 1} \\ &= \frac{V}{\pi^2}\left(\frac{k_BT}{\hbar c}\right)^3 \sum_{n=1}^{\infty}\int_0^\infty \exp(-nu)u^2\,\mathrm{d}u = \frac{V}{\pi^2}\left(\frac{k_BT}{\hbar c}\right)^3 \sum_{n=1}^{\infty}\frac{2}{n^3} \\ &= \frac{2\zeta(3)V}{\pi^2}\left(\frac{k_BT}{\hbar c}\right)^3,\end{aligned}$$

where $\zeta(3) = \sum_{n=1}^{\infty} n^{-3} = 1.202\ldots$ A cavity of a volume of 1 $\mathrm{cm}^3$ thus contains $5.46 \times 10^8$ photons on average.

**Problem 12.8.**

*The spectrum of light emitted by a star peaks at a wavelength of* 750 nm. *What is the surface temperature of the star? The star can be approximated by a blackbody.*

The energy flux density of isotropic radiation is given by $j = cu/4$, where $c$ is the speed of light and $u$ is the density of the internal energy. Each narrow frequency interval $\mathrm{d}\omega$ thus carries the energy flux density of $\mathrm{d}j = (c\hbar\omega/4V)\,\mathrm{d}N(\omega)$, where $V$ is the volume and

$$\mathrm{d}N(\omega) = \frac{1}{\exp(\beta\hbar\omega) - 1}\frac{Vq^2\,\mathrm{d}q}{\pi^2} = \frac{1}{\exp(\beta\hbar\omega) - 1}\frac{V\omega^2\,\mathrm{d}\omega}{\pi^2c^3}$$

is the average number of photons in this interval. Here, we took into account the dispersion relation $\omega = cq$ ($q$ denoting the wavevector), two independent polarizations of light, and the fact that linearly independent waves occupy only one octant of the reciprocal space. Thus

$$\frac{\mathrm{d}j}{\mathrm{d}\omega} = \frac{\hbar\omega^3}{4\pi^2c^2[\exp(\beta\hbar\omega) - 1]}\,.$$

Now we translate this expression into $\mathrm{d}j/\mathrm{d}\lambda$ since the peak of the spectral density is specified in terms of wavelength rather than frequency. By writing $\omega = 2\pi c/\lambda$ we have

$$\frac{\mathrm{d}j}{\mathrm{d}\lambda} = \frac{\mathrm{d}j}{\mathrm{d}\omega}\left|\frac{\mathrm{d}\omega}{\mathrm{d}\lambda}\right| = \frac{\mathrm{d}j}{\mathrm{d}\omega}\frac{2\pi c}{\lambda^2}$$

and

$$\frac{\mathrm{d}j}{\mathrm{d}\lambda} = \frac{(2\pi c)^2\hbar}{\lambda^5[\exp(2\pi\beta\hbar c/\lambda) - 1]} .$$

This is Planck's law. The peak at $\lambda_0$ is found by setting $\mathrm{d}(\mathrm{d}j/\mathrm{d}\lambda)/\mathrm{d}\lambda = 0$, which leads to the nonlinear equation $5[1 - \exp(-x)] = x$, where $x = 2\pi\beta\hbar c/\lambda$. The equation can be solved numerically, e.g., iteratively, but it is easy to see that $x \approx 5$. The exact solution is $x_0 = 4.965$, which results in the surface temperature of the star of

$$T = \frac{2\pi\hbar c}{\lambda_0 k_B x_0} = 3870\ \mathrm{K} .$$

This result is Wien's displacement law, which relates the position of the spectral peak to the temperature of the blackbody. Usually it is written as $\lambda_0 T = k_W$, where $k_W = 2\pi\hbar c/k_B x_0 = 2.9 \times 10^{-3}$ mK is the Wien's displacement constant.

**Problem 12.9.**
*Find the adiabatic compressibility of a polarized two-dimensional photon gas at* 300 K*!*

We follow the notation and the approach of Problem 12.7. In two dimensions, the summation over allowed wavevectors (radiation eigenmodes) is converted into an integral as $\sum_j \to (A/2\pi)\int_0^\infty q\mathrm{d}q$ (valid for a single polarization of light). By setting $\Omega = -\gamma A$, where $\gamma$ and $A$ denote the surface tension (i.e., pressure in two dimensions) and the surface area of the photon gas, respectively, we have

$$\begin{aligned}\beta\gamma A &= -\frac{A}{2\pi}\int_0^\infty \ln\bigl(1 - \exp(-\beta\hbar c q)\bigr) q\mathrm{d}q = \ldots\\ &= \frac{A\zeta(3)}{2\pi(\beta\hbar c)^2} = -\beta\Omega .\end{aligned}$$

We retraced all the steps of the analogous calculation in three dimensions. To calculate the adiabatic compressibility, we need the entropy of the photon gas as a function of $\gamma = \zeta(3)(k_B T)^3/2\pi(\hbar c)^2$ and $A$:

$$S = -\left(\frac{\partial\Omega}{\partial T}\right)_A = \frac{3\zeta(3)Ak_B^3T^2}{2\pi(\hbar c)^2} \propto AT^2 \propto A\gamma^{2/3} .$$

(In two dimensions, the equation of a reversible adiabatic process in a photon gas reads $\gamma A^{3/2} = \mathrm{const.}$, whereas in three dimensions, it is $pV^{4/3} = \mathrm{const.}$; see

Problem 4.18.) By differentiating $S(\gamma, A)$ we obtain the final result:

$$\begin{aligned}\chi_S &= -\frac{1}{A}\left(\frac{\partial A}{\partial p}\right)_S = \frac{2}{3\gamma} = \frac{4\pi(\hbar c)^2}{3\zeta(3)(k_B T)^3} \\ &= 4.9 \times 10^{10}\ \mathrm{m/N}\,.\end{aligned}$$

**Problem 12.10.**

*What is the chemical potential of the free electron gas in silver at absolute zero? Calculate the pressure and the isothermal compressibility of this Fermi gas! The density and the kilomolar mass of silver are* 10500 kg/m$^3$ *and* 107.9 kg/kmol, *respectively; there is one conduction electron per atom.*

The chemical potential of electrons at absolute zero $\mu(0)$ is obtained by realizing that the occupation number

$$f(\mu, E) = \frac{1}{\exp\big((E-\mu)/k_B T\big) + 1}$$

is equal to 1 in all states with energy smaller than $\mu(0)$ and 0 otherwise. We recall that the density of states of free electrons with $E = \hbar^2 q^2/2m$ and twofold spin degeneracy is equal to

$$g(E) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}\,,$$

and we obtain

$$N = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^{\mu(0)} E^{1/2}\,\mathrm{d}E = \frac{V}{3\pi^2}\left[\frac{2m\mu(0)}{\hbar^2}\right]^{3/2}$$

or

$$\mu(0) = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3} = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 Z N_A \rho}{M}\right)^{2/3} = 5.50\ \mathrm{eV}\,,$$

where $Z$ is the number of conduction electrons per atom.

The isothermal compressibility of the electron gas is obtained from the equation of state which, in turn, follows from the grand canonical partition function since $\Omega = -pV$. Therefore we first calculate the grand potential:

$$\begin{aligned}\beta\Omega &= -\frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \ln\Big(1+\exp\big(\beta(\mu - E)\big)\Big)E^{1/2}\,\mathrm{d}E \\ &= -\frac{V}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\Bigg[E^{3/2}\ln\Big(1+\exp\big(\beta(\mu-E)\big)\Big)\Big|_0^\infty \\ &\qquad + \beta\int_0^\infty \frac{E^{3/2}\mathrm{d}E}{\exp\big(\beta(E-\mu)\big)+1}\Bigg]\,.\end{aligned}$$

The first term of the above result is obtained by integration by parts and is equal to 0, which can be easily seen by applying L'Hôpital rule. The second term contains $f(\mu, E)$ which reduces to a step function at absolute zero. Thus $pV = \left(2V/15\pi^2\right)\left(2m/\hbar^2\right)^{3/2}\mu^{5/2}(0)$ and finally

$$p = \frac{2N\mu(0)}{5V}$$

with

$$\chi_T = \frac{3}{5p},$$

where we took into account that $\mathrm{d}\mu(0)/\mathrm{d}V = -2\mu(0)/3V$.

The pressure of the gas of conduction electrons in silver is $2.05 \times 10^{10}$ Pa and the isothermal compressibility is $2.92 \times 10^{-11}$ Pa$^{-1}$. This value exceeds the reciprocal Young's modulus of silver equal to $1.21 \times 10^{-11}$ Pa$^{-1}$ at room temperature.

**Problem 12.11.**

*Assume that at low temperatures, the occupation number in a Fermi gas of the conduction electrons in a metal can be approximated by*

$$f(\mu, E) = \begin{cases} 1, & E < \mu - \delta \\ 1/2 - (E-\mu)/2\delta, & \mu - \delta < E < \mu + \delta \\ 0, & E > \mu + \delta \end{cases},$$

*where $\delta = 3k_BT$. Calculate the change of the Fermi energy in caesium after it is heated from* 0 to 500 K; *at absolute zero it is equal to* 1.58 eV.

Within this model of the occupation number depicted in Fig. 12.3, the number of electrons $N = \int_0^\infty f(\mu, E)g(E)\,\mathrm{d}E$ is equal to

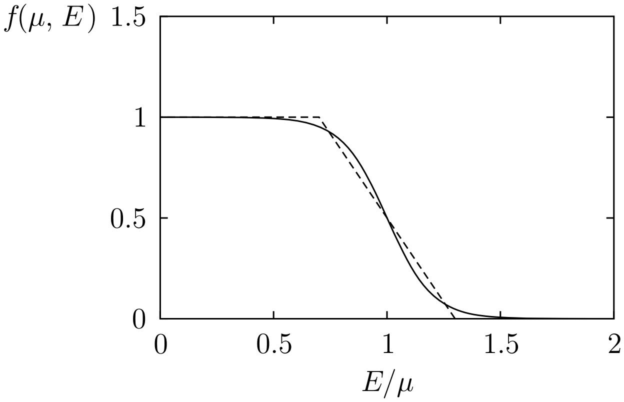

**Fig. 12.3** A simple model of the fermion occupation number at finite temperatures (dashed line) and the corresponding exact occupation number (solid line) at $T = 0.1\,\mu/k_B$

$$\begin{aligned} N &= \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left[\int_0^{\mu-\delta} E^{1/2}\,\mathrm{d}E + \int_{\mu-\delta}^{\mu+\delta}\left(\frac{1}{2}-\frac{E-\mu}{2\delta}\right)E^{1/2}\,\mathrm{d}E\right] \\ &= \frac{V}{3\pi^2}\left(\frac{2m\mu}{\hbar^2}\right)^{3/2}\left\{(1-u)^{3/2}-\frac{3}{10u}\left[(1+u)^{5/2}-(1-u)^{5/2}\right]\right. \\ &\qquad \left. +\frac{1}{2}\left(1+\frac{1}{u}\right)\left[(1+u)^{3/2}-(1-u)^{3/2}\right]\right\}, \end{aligned}$$

where $u = \delta/\mu$. A more transparent form is obtained by expanding the expression in the curly brackets for $u \ll 1$, which leads to

$$N = \frac{V}{3\pi^2}\left(\frac{2m\mu}{\hbar^2}\right)^{3/2}\left[1+\frac{1}{8}u^2+\mathcal{O}(u^4)\right].$$

Given that $\left(3\pi^2 N/V\right)^{2/3}\hbar^2/2m$ is the chemical potential at $T = 0$, the above result can also be rewritten as $\mu^{3/2}(0) = \mu^{3/2}\left(1+u^2/8\right)$ so that

$$\mu(T) = \mu(0)\left(1-\frac{u^2}{12}\right) \approx \mu(0)\left\{1-\frac{3}{4}\left[\frac{k_BT}{\mu(0)}\right]^2\right\}.$$

Finally, we replaced $\mu(T)$ in the correction term by $\mu(0)$, which is only slightly smaller; we also inserted $\delta = 3k_BT$. The resulting temperature dependence of the Fermi energy at low temperatures is qualitatively correct. By using the simple model of the occupation number with $\delta = 3k_BT$, we merely misunderestimate the magnitude of the finite-temperature correction: The more accurate Sommerfeld expansion yields $\pi^2/12 \approx 0.82246$ instead of 3/4. Our result predicts that the chemical potential of caesium at 500 K is smaller than at absolute zero by 0.883 meV.

**Problem 12.12.**

*The magnetic phenomena in the electron gas are due to the spins of electrons. Calculate the surface density of the magnetic dipole moment in a two-dimensional electron gas at* 6000 K *after a* 10 T *magnetic field is switched on! At this temperature, the chemical potential of this gas is equal to* 5 eV *in zero field. By how much would it change if the gas were exposed to a field of* $10^5$ T*? (Fields so strong are thought to exist in the atmosphere of neutron stars.) The mass of electron is* $9.1\times10^{-31}$ kg *and the Bohr magneton is* $p_B = 9.27\times10^{-24}$ Am$^2$.

In a magnetic field of magnetic flux density $B$, the energy of electrons consists of the kinetic energy as well as of the interaction between the electron spin and the field which reads $\pm p_B B$ (Fig. 12.4). We took into account that the magnitude of spin is 1/2 and that the gyromagnetic ratio of the electron is $2p_B/\hbar$. The sign of the interaction energy depends on the orientation of the spin with respect to the field. As a result, the numbers of electrons oriented along the field ($N_+$) and in the opposite direction ($N_-$) are different. This difference is manifested as a nonzero magnetization

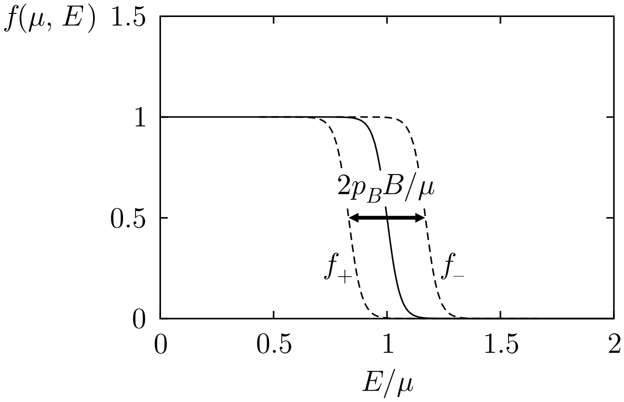

**Fig. 12.4** Fermi–Dirac distribution as a function of energy (solid line). The width of the step at $E \approx \mu$ is approximately equal to $2k_BT$. Once the magnetic field is switched on, the energy of electrons also depends on the orientation of the spin. The distributions $f_-$ and $f_+$ corresponding to spin down and up, respectively, are shifted by $\pm p_B B$ with respect to the zero-field distribution $f(B = 0)$ (dashed lines)

$M = p_B|N_+ - N_-|/A$ (here given per unit surface area $A$); this is referred to as the Pauli paramagnetism. The number of electrons in zero field is equal to

$$N = g\int_0^\infty \frac{\mathrm{d}E}{1 + \exp\big(\beta(E-\mu)\big)} = gk_BT \ln\big(1 + \exp(\beta\mu)\big),$$

where $g = mA/\pi\hbar^2$ is the density of states in two dimensions, $\mu$ is the chemical potential in zero field, and $m$ is the electron mass. After the magnetic field is turned on, the above result is replaced by

$$N_\pm = \frac{gk_BT}{2}\ln\Big(1 + \exp\big(\beta(\mu \mp p_B B)\big)\Big).$$

Now this is used to calculate the magnetization:

$$\begin{aligned} M &= \frac{gp_Bk_BT}{2A}\ln\left(\frac{1 + \exp\big(\beta(\mu + p_B B)\big)}{1 + \exp\big(\beta(\mu - p_B B)\big)}\right) \\ &\approx \frac{mp_B^2 B}{\pi\hbar^2} = 2.24 \times 10^{-8}\ \mathrm{A}. \end{aligned}$$

We took into account that $\exp\big(\beta(\mu \pm p_B B)\big) \gg 1$ and $p_B B \ll \mu$.

In the above derivation we assumed that the chemical potential is only negligibly altered by the magnetic field, which is not the case in extremely strong fields. The chemical potential $\mu_f$ in a strong field of $10^5$ T is obtained by requiring that the total number of fermions $N = N_+ + N_-$ be conserved:

$$\ln\bigl(1+\exp(\beta\mu)\bigr) = \frac{1}{2}\ln\Bigl(\bigl[1+\exp\bigl(\beta(\mu_f + p_B B)\bigr)\bigr] \times \bigl[1+\exp\bigl(\beta(\mu_f - p_B B)\bigr)\bigr]\Bigr).$$

We introduce $u = \exp(\beta\mu_f)$ and obtain a quadratic equation

$$u^2 + 2u\cosh(\beta p_B B) + 1 - \bigl[1+\exp(\beta\mu)\bigr]^2 = 0\,.$$

The physically relevant solution of this equation is $u = 3220$, which yields $\mu_f = 4.18$ eV. Despite the rather high temperature, the nonrelativistic treatment of the electron gas was appropriate since both $k_B T \approx 0.5$ eV and $\mu = 5$ eV are much smaller than the rest energy of the electron of 0.511 MeV.

**Problem 12.13.**
*Calculate the chemical potential of the free electron gas in a white dwarf star of density* $10^9$ kg/m$^3$ *and temperature* $10^5$ K*! Such a star can be regarded as a mixture of helium nuclei and electrons. Should the electrons be treated as relativistic particles? What is the average energy of electrons?*

This case differs from that in Problem 12.10 only in the energy–momentum relation $E(p)$ which is relativistic:

$$E^2 = m^2c^4 + p^2c^2\,.$$

It is convenient to introduce a new variable $u$ so that $\sinh u = p/mc$; then $E = mc^2\cosh u$. The number of states within an interval of width of d$p$ is

$$\frac{8\pi V}{h^3}p^2\,\mathrm{d}p = \frac{8\pi V m^3c^3}{h^3}\sinh^2 u\,\cosh u\,\mathrm{d}u\,,$$

and the chemical potential is determined by

$$N = \frac{8\pi V m^3 c^3}{h^3}\int_0^\infty \frac{\sinh^2 u\,\cosh u\,\mathrm{d}u}{\exp\bigl(\beta(mc^2\cosh u - \mu)\bigr)+1}\,.$$

We assume that the electron gas is strongly degenerate so that $k_B T \ll \mu$, and we calculate the chemical potential at absolute zero:

$$N = \frac{8\pi V m^3c^3}{h^3}\int_0^{u_0}\sinh^2 u\,\cosh u\,\mathrm{d}u = \frac{8\pi V m^3c^3}{3h^3}\sinh^3 u_0\,.$$

From this relation we express $u_0$ and insert it into $\mu(0) = mc^2\cosh u_0$ to find that

$$\mu(0) = mc^2\sqrt{1+\left(\frac{3N}{8\pi V}\right)^{2/3}\frac{h^2}{m^2c^2}}\,.$$

At low number densities $N/V$, $\mu(0) \approx mc^2 + (3N/8\pi V)^{2/3}\, h^2/2m$, which agrees with the result of Problem 12.10. The number density of electrons inside a white dwarf is $3 \times 10^{35}/\mathrm{m}^3$ (two electrons per one helium atom) so that the chemical potential is 0.657 MeV, which is not too far from the rest energy of the electron of $mc^2 = 0.511$ MeV. In this case, a nonrelativistic analysis would evidently produce a result not too far from the correct one. We also note that the characteristic temperature corresponding to these energies is $\sim 10^9$ K, which is much more than the actual temperature of the white dwarf. This comparison justifies our treating the electron gas as if it were at absolute zero.

The average particle energy in a highly degenerate electron gas at absolute zero is

$$\begin{aligned}\frac{\langle E\rangle}{N} &= \frac{8\pi V m^4 c^5}{N h^3}\int_0^{u_0} \sinh^2 u \cosh^2 u \,\mathrm{d}u \\ &= \frac{\pi}{4}\frac{V}{N}\frac{m^4c^5}{h^3}(\sinh 4u_0 - 4u_0) = \frac{3}{32}\frac{\sinh 4u_0 - 4u_0}{\sinh^3 u_0}\, mc^2 \,.\end{aligned}$$

From $\cosh u_0 = \mu(0)/mc^2$ we obtain $u_0 = 0.739$, yielding $\langle E\rangle/N = 0.602$ MeV. From this result we subtract the rest energy so as to obtain the kinetic energy, and compare the kinetic energy with $\mu(0) - mc^2$. The ratio

$$\frac{\langle E\rangle/N - mc^2}{\mu(0) - mc^2} = 0.623$$

differs only slightly from the nonrelativistic result of $3/5$.

**Problem 12.14.**

*Calculate the pressure of the free electron gas in a white dwarf star! The electrons should be treated relativistically, whereas their distribution over energy levels can be assumed to be the same as at absolute zero. The electron density is* $3 \times 10^{35}\ \mathrm{m}^{-3}$.

The pressure can be obtained just like in Problem 12.10. When calculating the grand potential, we introduce the same reduced variable as in Problem 12.13 and we integrate by parts:

$$\begin{aligned}\beta\Omega &= -\frac{8\pi V m^3 c^3}{h^3}\int_0^\infty \ln\Big(1 + \exp\big(\beta(\mu - mc^2\cosh u)\big)\Big)\sinh^2 u \cosh u \,\mathrm{d}u \\ &= -\frac{8\pi V m^3 c^3}{h^3}\left[\frac{\sinh^3 u}{3}\ln\Big(1 + \exp\big(\beta(\mu - mc^2\cosh u)\big)\Big)\Big|_0^\infty \right. \\ &\qquad \left. + \frac{\beta mc^2}{3}\int_0^\infty \frac{\sinh^4 u \,\mathrm{d}u}{\exp\big(\beta(mc^2\cosh u - \mu)\big) + 1}\right].\end{aligned}$$

The first term is equal to 0, whereas at $T = 0$ the second one gives

$$\begin{aligned}\beta\Omega &= -\frac{8\pi V m^4 c^5}{3h^3 k_B T}\int_0^{u_0}\sinh^4 u\,\mathrm{d}u \\ &= -\frac{2\pi V m^4 c^5}{3h^3 k_B T}\left(\sinh^3 u_0\cosh u_0 - \frac{3}{2}\sinh u_0\cosh u_0 + \frac{3}{2}u_0\right).\end{aligned}$$

Here $u_0$ is determined by $\sinh^3 u_0 = 3Nh^3/8\pi V m^3 c^3$ (Problem 12.13); at $N/V = 3\times 10^{35}$ m$^{-3}$, $u_0 = 0.739$. The pressure follows from $\Omega = -pV$ and is equal to $2.74\times 10^{21}$ Pa.

**Problem 12.15.**

*Calculate the heat capacity of a degenerate ultrarelativistic electron gas at* $10^{10}$ K *and density* $3.5\times 10^{10}$ kg/m$^3$*! The energy of the electrons is given by* $E = cp$*, where* $c$ *stands for the speed of light and* $p$ *is the linear momentum. Use the low-temperature (Sommerfeld) expansion*

$$\int_0^\infty h(E)f(E)\,\mathrm{d}E = \int_0^\mu h(E)\,\mathrm{d}E + \frac{\pi^2}{6}(k_B T)^2\frac{\mathrm{d}h}{\mathrm{d}E}\bigg|_\mu + \dots,$$

*where* $f(E)$ *is the Fermi occupation number,* $h(E)$ *is a continuous differentiable function at* $E = \mu$*, and* $\mu$ *is the chemical potential.*

We start by identifying the density of states $g(E)$ for ultrarelativistic electrons. Using the Bohr–Sommerfeld rule, a sum over single-electron states can be replaced by an integral over the phase space:

$$\sum \to 2\int \frac{\mathrm{d}\mathbf{r}\,4\pi p^2\mathrm{d}p}{h^3} = \frac{V}{\pi^2\hbar^3 c^3}\int E^2\mathrm{d}E = \int g(E)\,\mathrm{d}E\,,$$

where $g(E) = VE^2/\pi^2(\hbar c)^3$; the spin degeneracy is taken into account.

To obtain the heat capacity, we first need to calculate the average (internal) energy $\langle E\rangle = \int_0^\infty f(E)g(E)E\,\mathrm{d}E$. The Sommerfeld expansion will evidently give $\langle E\rangle$ which will depend on temperature both explicitly and through $\mu$, which itself depends on temperature. Thus $\mu(T)$ should be derived first by calculating the number of electrons, again using the Sommerfeld expansion

$$\langle N\rangle = \int_0^\infty f(E)g(E)\,\mathrm{d}E = \frac{V}{\pi^2(\hbar c)^3}\frac{\mu^3}{3}\left[1 + \pi^2\left(\frac{k_b T}{\mu}\right)^2\right],$$

with $h(E) = g(E)$. From here we express the chemical potential at $T = 0$:

$$\mu_0 = \hbar c\sqrt[3]{\frac{3\pi^2\langle N\rangle}{V}}\,,$$

whereas at finite temperatures

$$\mu(T) = \mu_0 \left[ 1 - \frac{\pi^2}{3} \left( \frac{k_B T}{\mu_0} \right)^2 \right] .$$

Here and below we assume that at low temperatures $\mu(T)$ and $\mu_0$ do not differ significantly.

The average energy is obtained by setting $h(E) = Eg(E)$ and reads

$$\begin{aligned} \langle E \rangle &= \frac{3}{4} \frac{\langle N \rangle \mu^4}{\mu_0^3} \left[ 1 + 2\pi^2 \left( \frac{k_B T}{\mu} \right)^2 \right] \\ &\approx \frac{3}{4} \langle N \rangle \mu_0 \left[ 1 + \frac{2\pi^2}{3} \left( \frac{k_B T}{\mu_0} \right)^2 \right] . \end{aligned}$$

Thus the heat capacity per particle is a linear function of temperature:

$$c = \frac{1}{\langle N \rangle} \frac{\mathrm{d}E}{\mathrm{d}T} = \frac{\pi^2 k_B^2 T}{\mu_0} .$$

Numerical results: $\mu_0 = 20.6\,\mathrm{MeV}$ (this is much larger than the rest energy of electron of 0.52 MeV, which justifies the ultrarelativistic limit used) and $c = 35.6\ \mu\mathrm{eV/K}$.

**Problem 12.16.**

*What is the Fermi energy of a two-dimensional free electron gas at absolute zero and at* 200 K*? What is the lowest temperature such that the occupation probability for all electron levels is less than* 0.5*? The density of electrons equals* $10^{17}/\mathrm{m}^2$.

The chemical potential of electrons is implicitly determined by the relation $N = \int_0^\infty f(\mu, E) g(E)\, \mathrm{d}E$, where $N$ is the number of electrons,

$$f(\mu, E) = \left[ \exp\bigl( (E - \mu)/k_B T \bigr) + 1 \right]^{-1}$$

is their occupation number, and $g(E)$ is the density of states. In two dimensions the latter is given by

$$g(E) = \frac{mA}{\pi \hbar^2} ,$$

where $A$ denotes the surface area of the system. Then

$$\begin{aligned} N &= \frac{mA}{\pi\hbar^2} \int_0^\infty \frac{\mathrm{d}E}{\exp\bigl( (E-\mu)/k_B T \bigr) + 1} \\ &= \frac{mAk_B T}{\pi\hbar^2} \int_{-\mu/k_B T}^\infty \frac{\mathrm{d}u}{\exp u + 1} = \frac{mAk_B T}{\pi\hbar^2} \ln\left( 1 + \exp\left( \frac{\mu}{k_B T} \right) \right) , \end{aligned}$$

which gives

$$\mu(T) = k_B T \ln \left( \exp \left( \frac{\pi \hbar^2 N}{m A k_B T} \right) - 1 \right).$$

The temperature dependence of the chemical potential, which amounts to $N\pi\hbar^2/mA = 24.0$ meV at absolute zero and to 19.1 meV at 200 K, is shown in Fig. 12.5. As suggested by Problem 12.11, the behavior of the chemical potential of a three-dimensional electron gas is qualitatively similar in that $\mu(T)$ is a decreasing function with $\mu > 0$ at low temperatures whereas at high enough temperatures $\mu < 0$, which can be confirmed by a rigorous numerical calculation.

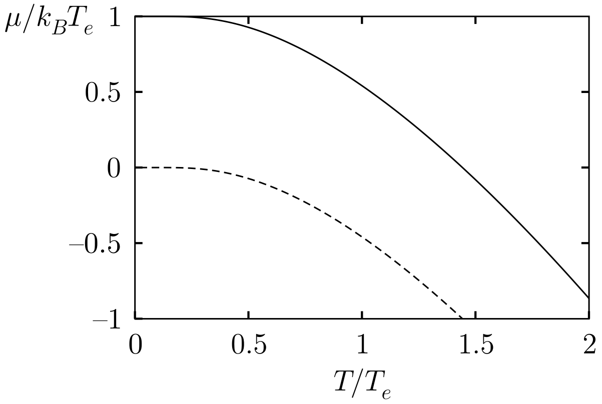

**Fig. 12.5** Temperature dependence of the chemical potential in a two-dimensional electron gas (solid line). In two dimensions the chemical potential of bosons with same characteristic temperature $T_e$ differs only by a constant offset (dashed line)

The numerical answer: The occupation number is equal to 0.5 at $E = \mu(T)$. Since $E > 0$, the occupation of each electron state will be below 0.5 at temperatures where $\mu(T) < 0$, that is for $T > T_e/\ln 2 = 401$ K. (Here $T_e = N\pi\hbar^2/mAk_B$ is the characteristic temperature.)

The above analysis can be easily extended to calculate the chemical potential of a two-dimensional boson gas: For particles with spin $j$ one has

$$\mu(T) = k_B T \ln \left( 1 - \exp\left( -\frac{2\pi\hbar^2 N}{(2j+1)Amk_B T} \right) \right).$$

The characteristic temperature of a boson gas differs from $T_e$ because of the different spin degeneracy. The functional dependence of the chemical potential of bosons on temperature is the same as for fermions, the only difference lying in the additive constant which ensures that $\mu < 0$ so that the occupation number is positive for all boson states including those with $E = 0$ (Fig. 12.5).

**Problem 12.17.**
*At absolute zero, the surface tension of a two-dimensional electron gas is equal to* 10 N/m. *Calculate its value at* $10^6$ K*!*

In the partition function $\exp(-\beta\Omega) = \prod_{j=0}^{\infty}\left[1 + \exp\left(\beta(\mu - E_j)\right)\right]$, where the index $j$ runs over levels with energies $E_j$, the sum can be replaced by an integral and the discrete levels $E_j$ by a continuous variable $E$. Thus we find that the grand potential reads

$$\Omega = -k_B T \int_0^{\infty} \ln\Big(1 + \exp\big(\beta(\mu - E)\big)\Big)\, g(E)\, \mathrm{d}E\,,$$

where $g(E) = mA/\pi\hbar^2$ is the density of states of a free particle in two dimensions (below denoted by $g$ alone because it does not depend on $E$) and $E = \hbar^2 q^2/2m$ is the kinetic energy; $m$ stands for the mass of electron, $q$ for the wavevector, and $A$ for the surface area occupied by the electrons. The surface tension of the gas $\gamma$ is obtained from the grand potential $\Omega = -\gamma A = -k_B T I(T)$. Here $I(T)$ is a dimensionless integral which can be integrated by parts:

$$\begin{aligned} I(T) &= g\int_0^{\infty} \ln\Big(1 + \exp\big(\beta(\mu - E)\big)\Big)\,\mathrm{d}E \\ &= gE\ln\Big(1 + \exp\big(\beta(\mu - E)\big)\Big)\Big|_0^{\infty} + g\int_0^{\infty} \frac{\beta E\,\mathrm{d}E}{1 + \exp\big(\beta(E - \mu)\big)}\,. \end{aligned}$$

The first term is 0 both at the upper and at the lower bound, which can be seen by applying the L'Hôpital rule. The remaining integral can now be calculated at $T = 0$.

The Fermi distribution is replaced by a step function so that

$$I(0) = g\int_0^{\mu_0} \beta E\,\mathrm{d}E = (g\beta\mu_0^2/2) = \beta N^2/2g.$$

The chemical potential is determined by the number of electrons in the system: $N = \int_0^{\mu_0} g\,\mathrm{d}E = g\mu_0$. We finally find that at $T = 0$

$$\gamma(0) = \frac{\pi N^2\hbar^2}{2mA^2}$$

and $\mu_0 = \hbar[2\pi\gamma(0)/m]^{1/2} = 5.5$ eV. At $T = 10^6$ K, on the other hand, $\beta\mu \ll 0$ and the entire analysis can be performed in the high-temperature limit where even at the lowest energies, one can write $\ln\Big(1 + \exp\big(\beta(\mu - E)\big)\Big) \approx \exp\big(\beta(\mu - E)\big)$. Then

$$I(T) = g\int_0^{\infty} \exp\big(\beta(\mu - E)\big)\,\mathrm{d}E = gk_B T\exp(\beta\mu)\,.$$

The chemical potential is again found by requiring that

$$N = \int_0^\infty \frac{g\,\mathrm{d}E}{\exp\big(\beta(E-\mu)\big)+1}$$
$$\approx g\int_0^\infty \exp\big(\beta(\mu-E)\big)\,\mathrm{d}E = gk_BT\exp(\beta\mu)\,.$$

Thus

$$\gamma(T\to\infty) = \frac{Nk_BT}{A} = \frac{k_BT}{\hbar}\sqrt{\frac{2m\gamma(0)}{\pi}} = 315\ \mathrm{N/m}\,.$$

The high-temperature result is the classical ideal gas equation of state in two dimensions, which is reasonable since in this limit the occupation number is low for all electron states. The requirement that the particle number be conserved also implies that $N = g\mu_0 = gk_BT\exp(\beta\mu)$, or, at $10^6$ K, $\beta\mu = \ln(\beta\mu_0) = -2.75$ and $\mu = -237$ eV. This *a posteiori* justifies the high-temperature limit used above.

**Problem 12.18.**
*The conduction electrons in a thin layer of gallium arsenide deposited onto a silicon crystal behave like a two-dimensional system. Explore the asymptotic temperature dependence of the heat capacity of these electrons! What is their heat capacity at* 300 K*? The density of electrons is* $5\times10^{16}/\mathrm{m}^2$.

The average energy of electrons is

$$\langle E\rangle = \left(\frac{\partial\beta\Omega}{\partial\beta}\right)_{\beta\mu} = \frac{mA}{\pi\hbar^2}\int_0^\infty \frac{E\,\mathrm{d}E}{\exp\big(\beta(E-\mu)\big)+1}\,,$$

where we inserted the grand potential $\Omega$ given in Problem 12.17. The resulting integral is evaluated by keeping in mind that at high temperatures $\mu < 0$ so that the occupation number of all energy levels is small or $\exp\big(\beta(E-\mu)\big) \gg 1$. Then the denominator can be expanded, yielding

$$\langle E\rangle = \frac{mA}{\pi\hbar^2}\sum_{n=1}^{\infty}(-1)^{n-1}\int_0^\infty \exp\big(-n\beta(E-\mu)\big)E\,\mathrm{d}E$$
$$= \frac{mA}{\pi\hbar^2\beta^2}\sum_{n=1}^{\infty}\frac{(-1)^{n-1}}{n^2}\exp(n\beta\mu)\,.$$

Now we use $T_e$ to denote $N\pi\hbar^2/mAk_B$ and we recall that $\exp(\beta\mu) = \exp(T_e/T) - 1$ (Problem 12.16) so that

$$\langle E\rangle = Nk_BT_e\left(\frac{T}{T_e}\right)^2\sum_{n=1}^{\infty}\frac{(-1)^{n-1}}{n^2}\left[\exp\left(\frac{T_e}{T}\right)-1\right]^n.$$

Thus the heat capacity is equal to

$$C = Nk_B \sum_{n=1}^{\infty} \frac{(-1)^{n-1}\left[1-\exp\left(T_e/T\right)\right]^{n-1}}{n^2} \times \left[\left(2\frac{T}{T_e}-n\right)\exp\left(\frac{T_e}{T}\right)-2\frac{T}{T_e}\right]$$

$$= Nk_B\left[1-\frac{1}{36}\left(\frac{T_e}{T}\right)^2+\ldots\right].$$

The final result was obtained by Taylor-expanding $\exp\left(T_e/T\right)$; the second-order correction in $T_e/T$ contains contributions from terms with $n = 1, 2$, and 3. With the above data one has $T_e = 139$ K, yielding $\mu < 0$ for $T > T_e/\ln 2 = 200$ K. At 300 K we obtain $C/A = 6.86 \times 10^{-7}$ J/m$^2$K.

**Problem 12.19.**

*An electron gas with a Fermi energy of* 0.5 eV *is confined to a layer of thickness of* 1 nm. *Calculate the density of the gas at absolute zero! What is the density of the gas after the layer thickness is increased to* 2 nm *at a fixed Fermi energy, which is ensured by introducing additional electrons?*

The layer is a nearly two-dimensional system in that its thickness $d$ is finite but much smaller than its lateral dimensions. We choose the $z$-axis to point along the layer normal, and the $x$ and $y$ axes lie within the plane of the layer. The layer acts like an infinite potential well trapping the electrons. At absolute zero all possible energy levels where $E < \mu$ are occupied whereas those with $E > 0$ are unoccupied. Each energy level is characterized by a wavevector $\mathbf{q} = (q_x, q_y, q_z)$. The allowed values of $q_z$ are determined by the boundary conditions for the electron wavefunctions at the layer boundaries, yielding $q_z = n_z\pi/d$ ($n_z = 1, 2, \ldots$). On the other hand, as the lateral dimensions of the layer are much larger than its thickness $d$, the spacing of the allowed values of $q_x$ and $q_y$ in the reciprocal space is much smaller than $\pi/d$. Thus when counting the electron states, $q_x$ and $q_y$ can be treated as continuous variables whereas $q_z$ is a discrete variable.

The energy of an electron is given by

$$E = \frac{\hbar^2}{2m}\left(Q^2+q_z^2\right),$$

where $Q^2 = q_x^2 + q_y^2$. At $T = 0$, the energies of the occupied states extend up to the chemical potential $\mu$. To find the largest possible value of $n_z$ consistent with this restriction, we set $E \leq \mu$ and take $Q = 0$ to obtain $n_z \leq (d/\pi\hbar)\sqrt{2m\mu} = 1.15$: In other words, only states with $n_z = 1$ are occupied. The total number of electrons in states with $E \leq \mu$ and $q_z = \pi/d$ is equal to

$$N = \sum_{\mathbf{q}} f(E) = 2 \int \frac{\mathrm{d}x\mathrm{d}y\, \mathrm{d}q_x\mathrm{d}q_y}{(2\pi)^2} = \frac{A}{\pi} \int_0^{Q_{\max}} Q\, \mathrm{d}Q$$
$$= \frac{Am}{\pi\hbar^2} \int_{\hbar^2\pi^2/2md^2}^{\mu} \mathrm{d}E\,.$$

Hence

$$\frac{N}{V} = \frac{m\mu}{\pi\hbar^2 d} - \frac{\pi}{2d^3} = 5.1 \times 10^{26}\ \mathrm{m}^{-3}.$$

When the layer thickness is increased to $2d$, this increases the smallest $n_z$ to 2.3 so that both $n_z = 1$ and $n_z = 2$ states are allowed. Therefore

$$N' = \frac{A}{\pi} \left( \int_0^{Q_{\max}(n_z=1)} Q\, \mathrm{d}Q + \int_0^{Q_{\max}(n_z=2)} Q\, \mathrm{d}Q \right),$$

where

$$Q_{\max}(n_z) = \sqrt{\frac{2m\mu}{\hbar^2} - \frac{n_z^2\pi^2}{4d^2}}\,.$$

Finally, the density of electrons in the 2 nm-thick layer must be equal to

$$\frac{N'}{V} = \frac{m\mu}{\pi\hbar^2 d} - \frac{5\pi}{16d^3} = 1.1 \times 10^{27}\ \mathrm{m}^{-3}.$$

**Problem 12.20.**
*A nondegenerate ideal gas consisting of atoms with spin* $1/2$ *is in coexistence with the condensed phase. After switching on a* 60 T *magnetic field at* 300 K, *the density of the gas increases by* $0.1\%$. *By how much does the chemical potential of the gas change in this process? Calculate the corresponding change of internal energy! The gyromagnetic ratio is* $2p_B/\hbar$, *the Bohr magneton* $p_B = 9.27 \times 10^{-24}$ Am$^2$; *both the temperature and the volume of the gas are fixed.*

The number of atoms of gas is not fixed because the gas is in a dynamic equilibrium with the condensed phase and exchanges atoms with it. Apart from the kinetic term, the energy of atoms contains the magnetic term $-\gamma\hbar j_z B$, where $\gamma$ denotes the gyromagnetic ratio and $j_z$ the projection of the spin onto the direction of the field. Since the gas is nondegenerate, the Pauli exclusion principle does not apply so that the partition function for $N$ atoms with a spin $j$ is given by

$$\exp\left(-\beta\Omega\right) = \sum_{N=0}^{\infty} \frac{\exp\left(\beta\mu N\right)}{h^{3N} N!} \left[ \sum_{j_z=-j}^{j} \int_V \mathrm{d}\mathbf{r} \int \exp\big(-\beta E(\mathbf{p}, j_z)\big)\, \mathrm{d}\mathbf{p} \right]^N,$$

where $E(\mathbf{p}, j_z) = p^2/2m - \gamma\hbar j_z B$ and $\mu$ is the chemical potential. We use $a$ as a shorthand for $\gamma\hbar B$ for brevity, integrate over the volume and the momenta, calculate the arithmetic sum over $j_z$, and obtain

$$\begin{aligned}\exp(-\beta\Omega) &= \sum_{N=0}^{\infty} \frac{\exp(\beta\mu N) V^N}{h^{3N} N!} \\ &\quad \times \left(\frac{2\pi m}{\beta}\right)^{3N/2} \left[\frac{\sinh\left(\beta a(j+1/2)\right)}{\sinh(\beta a/2)}\right]^N \\ &= \exp\left(\frac{V\exp(\beta\mu)}{\left(\beta h^2/2\pi m\right)^{3/2}} \frac{\sinh\left(\beta a(j+1/2)\right)}{\sinh(\beta a/2)}\right).\end{aligned}$$

In the last step, we recognize that the sum over $N$ is the Taylor series of an exponential function. Now we can express the grand potential $\Omega$: After inserting $j = 1/2$ we have

$$\beta\Omega = -2V\exp(\beta\mu)\left(\frac{2\pi m}{\beta h^2}\right)^{3/2} \cosh\left(\frac{\beta a}{2}\right).$$

The number density of the gas is calculated from the differential $\mathrm{d}\beta\Omega = \langle E\rangle\,\mathrm{d}\beta - \langle N\rangle\,\mathrm{d}\beta\mu - \beta p\,\mathrm{d}V + \beta V H\,\mathrm{d}B$, where $H$ is the strength of the magnetic field:

$$\begin{aligned}\langle n\rangle &= \frac{\langle N\rangle}{V} = -\frac{1}{V}\left(\frac{\partial\beta\Omega}{\partial\beta\mu}\right)_{\beta,V,B} \\ &= 2\exp(\beta\mu)\left(\frac{2\pi m}{\beta h^2}\right)^{3/2} \cosh\left(\frac{\beta a}{2}\right)\end{aligned}$$

and the internal energy $\langle E\rangle = (\partial\beta\Omega/\partial\beta)_{\beta\mu,V,B}$ reads

$$\begin{aligned}\langle E\rangle &= V\exp(\beta\mu)\left(\frac{2\pi m}{\beta h^2}\right)^{3/2}\left[3\beta^{-1}\cosh\left(\frac{\beta a}{2}\right) - a\sinh\left(\frac{\beta a}{2}\right)\right] \\ &= \frac{\langle n\rangle V}{2}\left[3\beta^{-1} - a\tanh\left(\frac{\beta a}{2}\right)\right].\end{aligned}$$

When the field is turned on at constant temperature and volume, the average density increases from $\langle n\rangle'$ to $\langle n\rangle$. This is accompanied by a change of chemical potential from $\mu'$ to $\mu$, where

$$\frac{\langle n\rangle}{\langle n\rangle'} = \exp\left(\beta(\mu - \mu')\right)\cosh\left(\frac{\beta a}{2}\right).$$

Therefore the change of the chemical potential is

$$\mu - \mu' = k_B T \ln\left(\frac{\langle n\rangle}{\langle n\rangle' \cosh(\beta a/2)}\right) \approx -2.1 \times 10^{-4}\,\mathrm{eV}.$$

The ratio of the internal energies with field on and in zero field is given by

$$\frac{\langle E\rangle}{\langle E\rangle'} = \frac{\langle n\rangle}{\langle n\rangle'}\left[1 - \frac{\beta a}{3}\tanh\left(\frac{\beta a}{2}\right)\right] \approx 0.99\,.$$

Thus the internal energy decreases by 1%.

**Problem 12.21.**
*By how much does the pressure of gaseous helium differ from that of a classical ideal gas at* 30 K *and number density of* $2 \times 10^{28}/\mathrm{m}^3$*? The angular momentum of helium atoms is* 0 *and its kilomolar mass is* 4 kg/kmol.

We first calculate the absolute activity of a classical ideal gas at the given conditions: $\exp(\beta\mu) = N\lambda_B^3/gV = 0.081$. Here

$$\lambda_B = \left(\frac{h^2}{2\pi m k_B T}\right)^{1/2}$$

is the thermal de Broglie wavelength and $g$ is the spin degeneracy $2j+1$ equal to 1 for helium. As the absolute activity is small, the chemical potential $\mu < 0$ and the occupation number is small in all states. In this limit, the chemical potential of the boson gas does not differ significantly from the chemical potential of the classical ideal gas and can be approximately determined by expanding the normalization integral in a power series in terms of the absolute activity. As illustrated in Fig. 12.6, this can be done by expanding the occupation number in terms of $\exp\bigl(-\beta(E-\mu)\bigr)$.

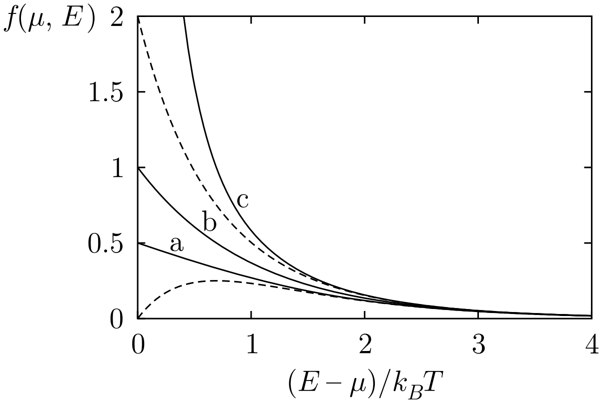

**Fig. 12.6** Occupation number of fermions (**a**), classical particles (**b**), and bosons (**c**) (solid lines), together with the approximate forms of the Fermi–Dirac and Bose–Einstein distributions, $\exp\bigl(-\beta(E-\mu)\bigr) \mp \exp\bigl(-2\beta(E-\mu)\bigr)$ (dashed lines). The smaller the chemical potential, the more accurate the approximations

The calculation can be carried out simultaneously for fermions (upper sign) and bosons (lower sign):

$$\begin{aligned}
N &= \frac{gV}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{E^{1/2}\,\mathrm{d}E}{\exp\big(\beta(E-\mu_\pm)\big)\pm 1} \\
&\approx \frac{gV}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left[\int_0^\infty E^{1/2}\exp\big(-\beta(E-\mu_\pm)\big)\,\mathrm{d}E\right. \\
&\qquad\qquad\left.\mp\int_0^\infty E^{1/2}\exp\big(-2\beta(E-\mu_\pm)\big)\,\mathrm{d}E\right] \\
&= \frac{gV}{\lambda_B^3}\left[\exp(\beta\mu_\pm)\mp\frac{\exp(2\beta\mu_\pm)}{2^{3/2}}\right],
\end{aligned}$$

where we took into account that $\int_0^\infty u^{1/2}\exp(-au)\,\mathrm{d}u = \sqrt{\pi}/2a^{3/2}$. Since the absolute activity of the classical ideal gas is $\exp(\beta\mu) = N\lambda_B^3/gV$, we have

$$\exp(\beta\mu_\pm) \approx \exp(\beta\mu) \pm \frac{\exp(2\beta\mu)}{2^{3/2}},$$

where $\mu$ is the chemical potential of the classical ideal gas whereas $\mu_+$ and $\mu_-$ are the chemical potentials of the fermion and boson gases, respectively. Upon inserting the given data, we find that $\mu_+$ and $\mu_-$ differ from $\mu$ by a mere 1.1%.

The equations of state for weakly degenerate fermion and boson gases are obtained from the grand potentials $\Omega_\pm = \mp\beta^{-1}\sum_j \ln\Big(1\pm\exp\big(\beta(\mu_\pm - E_j)\big)\Big)$ since $\Omega = -pV$. Thus

$$\begin{aligned}
\beta\Omega_\pm &= \mp\frac{gV}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty E^{1/2}\ln\Big(1\pm\exp\big(\beta(\mu_\pm-E)\big)\Big)\,\mathrm{d}E \\
&= \mp\frac{gV}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left[\underbrace{\frac{2E^{3/2}}{3}\ln\Big(1\pm\exp\big(\beta(\mu_\pm-E)\big)\Big)\Big|_0^\infty}_{=0}\right. \\
&\qquad\qquad\left.\pm\frac{2\beta}{3}\int_0^\infty\frac{E^{3/2}\exp\big(\beta(\mu_\pm-E)\big)\,\mathrm{d}E}{1\pm\exp\big(\beta(\mu_\pm-E)\big)}\right] \\
&\approx -\frac{gV}{\lambda_B^3}\left[\exp(\beta\mu_\pm)\mp\frac{\exp(2\beta\mu_\pm)}{2^{5/2}}\right].
\end{aligned}$$

[We took into account that $\int_0^\infty u^{3/2}\exp(-au)\,\mathrm{d}u = 3\sqrt{\pi}/4a^{5/2}$.] By recalling that $gV/\lambda_B^3 = N\exp(-\beta\mu)$ we finally have

$$p_\pm V = Nk_BT\left[\exp\big(\beta(\mu_\pm-\mu)\big)\mp\frac{\exp\big(\beta(2\mu_\pm-\mu)\big)}{2^{5/2}}\right]$$

$$\begin{aligned}&\approx Nk_BT\left[1\pm\frac{\exp(\beta\mu)}{2^{5/2}}\right]\\&=Nk_BT\left[1\pm\frac{N}{2^{5/2}gV}\left(\frac{h^2}{2\pi mk_BT}\right)^{3/2}\right]\end{aligned}$$

The pressure of a fermion gas is larger than the pressure of a classical gas at the same number density and temperature whereas the pressure of the boson gas is smaller than it; the magnitudes of the deviations are the same. Under the given conditions, the helium pressure is smaller than the pressure of a hypothetical classical gas with the same kilomolar mass and angular momentum by $1.19\times10^5$ Pa; the pressure of the hypothetical classical gas is $8.28\times10^6$ Pa.

**Problem 12.22.**

*At what temperature does liquid helium of a number density of* $2.2\times10^{28}/\mathrm{m}^3$ *undergo Bose–Einstein condensation? The angular momentum of helium atoms is* 0 *and the kilomolar mass is* 4 kg/kmol. *How does the number of particles in the ground state depend on temperature?*

When we evaluate the partition function by representing the density of states with a continuous function $g(E)$ which is proportional to $E^{1/2}$ for free particles with a dispersion relation $E=\hbar^2q^2/2m$, we make an error in that the zero-energy level is left out since $g(E=0)=0$. For fermions the error is irrelevant as the ground state cannot be occupied by more than $2j+1$ particles, $j$ being their spin, and this finite number is unimportant in the thermodynamic limit. In bosonic systems, on the other hand, a macroscopic number of particles can be accommodated in the ground state and thus the ground state must be included in the partition function. The total number of particles is therefore split into two terms:

$$N=N_0+N_>=\frac{1}{\exp(-\beta\mu)-1}+\sum_{E>0}\frac{1}{\exp\big(\beta(E-\mu)\big)-1}\,.$$

Condensation is observed when the number of particles in the ground state $N_0$ is comparable to the total number of particles, i.e., $N_0\sim N$. This means that the number of particles in states with $E>0$ denoted by $N_>$ is significantly smaller than $N$.

For the present purpose it is sufficient to estimate $N_>$. Since the energy of the ground state is 0, the chemical potential must be smaller than or equal to 0 at any temperature or else the occupation number of the ground state is negative, which makes no sense. If we assume that $\mu=0$, we overestimate the number of particles in states with $E>0$. For particles with angular momentum 0 we have

$$\begin{aligned}N_>&\le\frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty\frac{E^{1/2}\,\mathrm{d}E}{\exp(\beta E)-1}\\&=\frac{V}{4\pi^2}\left(\frac{2mk_BT}{\hbar^2}\right)^{3/2}\sum_{n=1}^{\infty}\int_0^\infty\exp(-nu)u^{1/2}\,\mathrm{d}u\end{aligned}$$

$$= \frac{V}{8\pi^{3/2}} \left( \frac{2mk_B T}{\hbar^2} \right)^{3/2} \sum_{n=1}^{\infty} n^{-3/2}$$
$$= 2.61\, V \left( \frac{2\pi mk_B T}{h^2} \right)^{3/2},$$

where we introduced $u = \beta E$ and we calculated the integral using the series expansion by taking into account that $\sum_{n=1}^{\infty} n^{-3/2} = \zeta(3/2) \approx 2.61238$. The total number of particles in the states with $E > 0$ is evidently finite and it increases with temperature so that at a low enough temperature, it will be smaller than the total number of particles. As a result, the remaining $N - N_>$ particles must be in the ground state. Thus we can define the critical temperature by requiring that $N_> = N$. This gives

$$T_c = \frac{h^2}{2\pi mk_B} \left( \frac{N}{2.61\, V} \right)^{2/3},$$

which yields 3.16 K for helium of a number density of $2.2 \times 10^{28}/\mathrm{m}^3$. Thus $N_> = N\,(T/T_c)^{3/2}$ and $N_0 = N\big[1 - (T/T_c)^{3/2}\big]$, which is valid only for $T \le T_c$; for $T > T_c$ the number of particles in the ground state is negligible (Fig. 12.7).

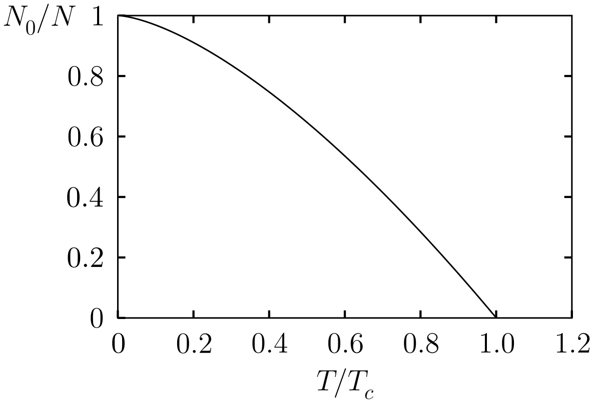

**Fig. 12.7** Relative number of particles in the ground state in an ensemble of free bosons versus temperature

A more elaborate analysis demonstrates that the chemical potential of the Bose–Einstein condensate below $T_c$ is indeed equal to 0. Using this result, it is easy to calculate the heat capacity of the condensate $C$. The particles in the ground state do not contribute to the internal energy so that

$$\langle E \rangle = \frac{V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \int_0^{\infty} \frac{E^{3/2}\, \mathrm{d}E}{\exp(E/k_B T) - 1}$$

$$= \frac{3}{2}\zeta\left(\frac{5}{2}\right) V \left(\frac{2\pi m}{h^2}\right)^{3/2} (k_B T)^{5/2}$$

and, consequently,

$$C = 5.03\, V \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} k_B$$
$$= 1.92\, N k_B \left(\frac{T}{T_c}\right)^{3/2},$$

where we inserted $\zeta(5/2) \approx 1.34149$. The heat capacity of the condensate is depicted in Fig. 12.8, which shows that close to the phase transition $C$ exceeds the high-temperature limit $1.5\, N k_B$; at the transition, it equals $1.92\, N k_B$. We thus realize that $C(T)$ is a non-monotonic function of temperature. A more accurate calculation where the heat capacity of the non-condensed phase with $\mu < 0$ is taken into account shows that $C(T)$ peaks right at the phase transition.

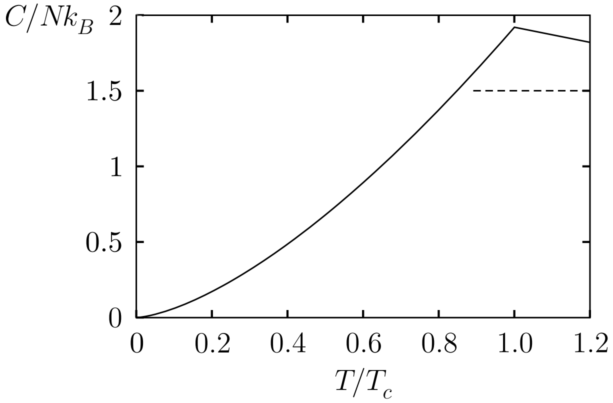

**Fig. 12.8** Temperature dependence of the heat capacity of the Bose–Einstein condensate (solid line); the formula derived for $T/T_c < 1$ is combined with results from the literature for $T/T_c > 1$. The high-temperature limit $C = 1.5\, N k_B$ is indicated by the dashed line

**Problem 12.23.**

*Show that a two-dimensional system of free bosons does not undergo Bose–Einstein condensation!*

In a Bose–Einstein condensate, the number of ground-level particles $N_0 = [\exp(-\beta\mu) - 1]^{-1}$ must be comparable to the total number of particles $N$. Thus we can estimate the chemical potential of the condensate by taking $N_0 \sim N$, which gives

$$\mu \approx -k_B T \ln\left(1 + \frac{1}{N}\right) \approx -\frac{k_B T}{N},$$

where we took into account that $N \gg 1$. Evidently, the chemical potential is of the order of $\mathcal{O}(1/N)$, which means that $\mu \to 0$ for large $N$. (This result was used in Problem 12.22.) Now recall that in two dimensions, one can analytically calculate the chemical potential of free bosons at any temperature as shown in Problem 12.16. A detailed examination of the result obtained in Problem 12.16 shows that for $T > 0$ the chemical potential does not contain any term of order of $\mathcal{O}(1/N)$ which leads us to conclude that in a two-dimensional system Bose–Einstein condensation does not take place.

**Problem 12.24.**

*A vessel with adsorbent-coated walls is filled with argon at* 20 °C *and* 1 bar. *Calculate the fraction of the adsorption centers that are occupied if the binding energy of an adsorbed atom is* 1 meV*! The kilomolar mass of argon is* 40 kg/kmol *and the angular momentum of argon atoms is zero.*

The grand canonical partition function for $N_0$ independent adsorption centers reads

$$\exp(-\beta\Omega) = \sum_N \exp\Big(\beta\big(\mu\sum_j N_j - \sum_j N_j E_j\big)\Big),$$

where the sums run over the possible numbers of adsorbed particles (0 and 1); the energy of an adsorption center is equal to the binding energy $-w$ if occupied and is 0 if empty. Therefore

$$\exp(-\beta\Omega) = \big[1 + \exp\big(\beta(\mu + w)\big)\big]^{N_0}.$$

The average number of centers that are occupied is given by the Fermi–Dirac distribution

$$\langle N\rangle = -\left(\frac{\partial\beta\Omega}{\partial\beta\mu}\right)_\beta = \frac{N_0}{\exp\big(-\beta(\mu + w)\big) + 1}.$$

In equilibrium, the chemical potential of the adsorbed atoms must be equal to the chemical potential of the gas inside the vessel given by $k_BT \ln\big(p/JT^{5/2}\big)$. Here

$$J = (2j + 1)\left(\frac{2\pi m}{h^2}\right)^{3/2} k_B^{5/2}$$

is the chemical constant; $m$ and $j$ are the mass and the angular momentum of an atom, respectively. Finally we have

$$\frac{\langle N\rangle}{N_0} = \left[\frac{JT^{5/2}}{p}\exp\left(-\frac{w}{k_BT}\right) + 1\right]^{-1} = 1.09 \times 10^{-7}.$$

**Problem 12.25.**

*Two plates coated with different adsorbents are immersed in a gas. The binding energies of atoms adsorbed on the first and on the second plate are equal to* 1 meV *and* 2 meV, *respectively. At* 150 K, 10% *of all adsorption centers on the first plate are occupied. What is the fraction of occupied adsorption centers on the second plate?*

The average occupancies of adsorption centers on the first and on the second plate are

$$x_1 = \frac{1}{\exp\left(-\beta(\mu_1 + w_1)\right) + 1}$$

and

$$x_2 = \frac{1}{\exp\left(-\beta(\mu_2 + w_2)\right) + 1},$$

respectively. Here, $-w_1 < 0$ and $-w_2 < 0$ are the corresponding binding energies, whereas $\mu_1$ and $\mu_2$ are the chemical potentials of the adsorbed atoms. The adsorbed atoms on the two plates are in equilibrium mediated by the gas so that $\mu_1 = \mu_2$. This gives

$$x_2 = \frac{1}{1 + \left(x_1^{-1} - 1\right)\exp\left(\beta(w_1 - w_2)\right)} = 0.107\,.$$

**Problem 12.26.**

*A sealed cylindrical vessel with adsorbent-coated walls contains a monatomic gas of kilomolar mass* 40 kg/kmol *at a temperature of* 100 K. *The vessel is rotated about its symmetry axis at an angular frequency of* $100\ \mathrm{s}^{-1}$. *What is the ratio of the relative magnitude of fluctuations of the number of adsorbed particles in a rotating and a nonrotating vessel? The radius of the vessel is* 1 m.

Like in Problem 12.24 the partition function for $N_0$ adsorption centers (which can be either occupied or empty) reads

$$\exp(-\beta\Omega) = \left[1 + \exp\left(\beta(\mu + w)\right)\right]^{N_0}\ ;$$

here $\mu$ is the chemical potential of adsorbed atoms and the binding energy of an adsorbed atom is $-w < 0$. The average number of adsorbed atoms is $\langle N\rangle = -\left(\partial\beta\Omega/\partial\beta\mu\right)_\beta = N_0/\left[\exp\left(-\beta(w+\mu)\right) + 1\right]$, whereas the fluctuations of the number squared are given by

$$\sigma_N^2 = \langle N^2\rangle - \langle N\rangle^2 = -\left(\frac{\partial^2\beta\Omega}{\partial(\beta\mu)^2}\right)_\beta = \frac{N_0\exp\left(-\beta(w+\mu)\right)}{\left[\exp\left(-\beta(w+\mu)\right) + 1\right]^2}\,.$$

Thus the relative magnitude of fluctuations is

$$\frac{\sigma_N}{\langle N\rangle}=\frac{\exp\left(-\beta(w+\mu)/2\right)}{\sqrt{N_0}}\,.$$

In equilibrium, the chemical potential of the adsorbed atoms $\mu$ is equal to the chemical potential of the atoms of the non-adsorbed gas $\mu_g$. In ideal monatomic gas,

$$\mu_g=k_BT\ln\left(\frac{p}{JT^{5/2}}\right),$$

where $J$ is the chemical constant. In a rotating vessel, the gas is redistributed by the centrifugal force: Close to the axis at $r=0$ the pressure is decreased, whereas at the wall at $r=R$ it is increased. Since an increase of pressure gives rise to an increase of the chemical potential of the gas at the wall, this implies an increase of occupancy of the adsorption centers, because in equilibrium $\mu=\mu_g(R)$. Now we need to find the change of the pressure of the gas at the wall.

Once equilibrium is established in the rotating vessel, the macroscopic material flow within it is zero, and thus the sum of the local chemical potential and of the centrifugal potential energy must be constant: $\mu_g(r)-m\omega^2r^2/2=const$. Here $\omega$ is the angular velocity, $m=M/N_A$ is the mass of a single atom; $M$ is the kilomolar mass of the gas and $N_A=6\times10^{26}$ kmol$^{-1}$. This gives

$$\mathrm{d}\mu_g(r)=m\omega^2r\,\mathrm{d}r\,.$$

Since at a constant temperature $\mathrm{d}\mu_g=k_BT\,\mathrm{d}p/p$, we further obtain

$$\frac{\mathrm{d}p}{p}=\frac{m\omega^2r\,\mathrm{d}r}{k_BT}\,.$$

The pressure profile thus reads

$$p(r)=p(0)\exp\left(\frac{m\omega^2r^2}{2k_BT}\right).$$

The integration constant $p(0)$ is determined by the constant mass constraint which implies that

$$\int_0^R p(r)r\,\mathrm{d}r=\frac{p_0R^2}{2}\,.$$

The left-hand and the right-hand side correspond to a rotating vessel and to a vessel at rest, respectively; $p_0$ is the uniform pressure in the vessel at rest. Thus the pressure at the wall is equal to

$$p(R)=p_0\frac{m\omega^2R^2/2k_BT}{1-\exp\left(-m\omega^2R^2/2k_BT\right)}\,.$$

With the given data we find that $p(R) = 1.126\, p_0$: The pressure at the wall is slightly increased due to rotation. Now we denote the difference of the chemical potentials at the wall in the rotating vessel and in the vessel at rest by $\Delta\mu_g(R)$. Finally we calculate the sought ratio which reads

$$\delta = \frac{(\sigma_N/\langle N\rangle)_\omega}{(\sigma_N/\langle N\rangle)_0} = \exp\left(-\beta\Delta\mu_g(R)/2\right) = \sqrt{\frac{p_0}{p(R)}} \approx 0.94\,.$$

In a rotating vessel, more atoms are adsorbed on the wall than in a vessel at rest and thus $\sigma_N/\langle N\rangle$ is smaller than in a vessel at rest.

Limiting cases: For $m\omega^2R^2/2k_BT \to 0$ (which corresponds to slow rotation, a small vessel, or a high temperature) we obtain the expected result $\delta \to 1$. On the other hand, for $m\omega^2R^2/2k_BT \to \infty$ (corresponding to fast rotation, a large vessel, or a low temperature) $p(R) \to \infty$ and $\delta \to 0$, since virtually all atoms are adsorbed.

**Problem 12.27.**
*After argon is pumped into a piece of porous glass, a fraction of the gas is adsorbed on the walls of the pores; the binding energy is* 0.1 eV *and the adsorbed atoms are free to move across the surface. What is the fraction of the adsorbed atoms at* 300 K*? How does the pressure of the non-adsorbed gas depend on temperature and volume? The kilomolar mass of argon is* 40 kg/kmol, *the angular momentum is* 0; *the number of atoms in the sample is* $2.4 \times 10^{19}$; *the total volume of the pores is* 1 $\mathrm{cm}^3$ *and their total surface area is* 1000 $\mathrm{m}^2$.

We start by estimating the absolute activity of the system by assuming that they are not adsorbed and by treating the atoms classically: In this case, the absolute activity is given by $\exp(\beta\mu_g) = N\left(h^2/2\pi mk_BT\right)^{3/2}/V$ and amounts to just $9.7 \times 10^{-8}$. Thus the occupancy of all energy levels is small and the non-adsorbed argon can be approximated by a classical gas. In equilibrium, the absolute activity of the adsorbed atoms will be small too and both subsystems—the adsorbed and the non-adsorbed gas—can be described by the Maxwell–Boltzmann distribution.

Since the adsorbed argon atoms can move freely along the walls of the pores, they behave like a two-dimensional classical ideal gas in a constant potential $-w$, where $-w < 0$ is the binding energy. The energy of an adsorbed atom is given by $E = \hbar^2q^2/2m - w$, and the total number of the adsorbed atoms is

$$N_a = \frac{2\pi mA}{h^2}\int_{-w}^{\infty} \exp\bigl(\beta(\mu_a - E)\bigr)\,\mathrm{d}E = \frac{2\pi mk_BTA}{h^2}\exp\bigl(\beta(\mu_a + w)\bigr)\,,$$

where we took into account that the spin degeneracy is 1; $A$ is the total pore surface area. Thus the chemical potential of the adsorbed atoms is

$$\mu_a = k_BT\ln\left(\frac{N_a\lambda_B^2}{A}\right) - w\,;$$

here $\lambda_B = \left(h^2/2\pi m k_B T\right)^{1/2}$ is the thermal de Broglie wavelength. The chemical potential of the $N_g$ non-adsorbed atoms is equal to

$$\mu_g = k_B T \ln\left(\frac{N_g \lambda_B^3}{V}\right),$$

where $V$ is the volume of the pores. In equilibrium $\mu_a = \mu_g$ or

$$\frac{N_a}{A}\exp\left(-\frac{w}{k_B T}\right) = \frac{N_g \lambda_B}{V}.$$

Since the total number of atoms is constant, we further have $N_a + N_g = N$ and thus

$$N_a = N\left[1 + \frac{V}{A\lambda_B}\exp\left(-\frac{w}{k_B T}\right)\right]^{-1} = 0.432\,N = 1.04 \times 10^{19}$$

and $N_g = N - N_a = 0.568\,N = 1.36 \times 10^{19}$. In the end, we reevaluate the absolute activities of the adsorbed and the non-adsorbed atoms with the revised input data again: $\exp(\mu_a/k_B T) = \exp(\mu_g/k_B T) = 5.5 \times 10^{-8} \ll 1$. This *a posteriori* justifies the assumptions made at the beginning.

The equation of state for the non-adsorbed gas is obtained by starting with the ideal gas law and inserting the volume- and temperature-dependent number of non-adsorbed atoms $N_g = N - N_a$. This gives

$$p = \frac{N_g k_B T}{V} = \frac{N k_B T}{V\left[1 + (A/V)\left(h^2/2\pi m k_B T\right)^{1/2}\exp\left(w/k_B T\right)\right]}.$$

**Problem 12.28.**
*Gaseous argon at* $27\,^\circ\mathrm{C}$ *and* $1$ bar *is kept in a container with adsorbing walls. The binding energy of an adsorbed atom is* $1$ meV. *What is the change of the relative magnitude of fluctuations of the energy of adsorbed atoms after a* $100$*-fold increase of pressure at a constant temperature? What is the entropy change per adsorption center? The kilomolar mass of argon is* $40$ kg/kmol *and its angular momentum is* $0$.

The adsorbed particle system is examined by considering the grand canonical ensemble. We use $N_0$ to denote the number of available adsorption centers and $-w < 0$ is the binding energy. The average energy is obtained from the partition function $\exp(-\beta\Omega)$ (see Problem 12.24)

$$\langle E\rangle = \left(\frac{\partial\beta\Omega}{\partial\beta}\right)_{\beta\mu} = -\frac{N_0 w}{\exp\left(-\beta(\mu + w)\right) + 1} = -\langle N\rangle w,$$

and the square of energy fluctuations reads

$$\sigma_E^2 = \langle E^2\rangle - \langle E\rangle^2 = -\left(\frac{\partial^2\beta\Omega}{\partial\beta^2}\right)_{\beta\mu} = \frac{N_0 w^2 \exp\left(-\beta(\mu + w)\right)}{\left[\exp\left(-\beta(\mu + w)\right) + 1\right]^2}.$$

Thus we have

$$\frac{\sigma_E}{\langle E\rangle} = \frac{1}{\sqrt{N_0}} \exp\left(-\frac{\beta(\mu + w)}{2}\right).$$

After the pressure of the non-adsorbed argon is increased, its chemical potential $\mu_g$ increases too. In equilibrium, it must be equal to the chemical potential of the adsorbed atoms, and thus the pressure increase translates into the change of occupancy of the adsorption centers. One has $\mu_g(T, p) = k_B T \ln(p/JT^{5/2})$, where $J = (2j + 1)(2\pi m)^{3/2} k_B^{5/2}/h^3 = 6.56 \times 10^5\ \mathrm{Pa/K^{5/2}}$ is the chemical constant, $m = M/N_A = 6.67 \times 10^{-26}$ kg is the mass of an argon atom, and $j$ is its angular momentum. For a 100-fold increase of pressure from $p'$ to $p$ we obtain

$$\frac{(\sigma_E/\langle E\rangle)_p}{(\sigma_E/\langle E\rangle)_{p'}} = \exp\left(\frac{\beta[\mu_g(T, p') - \mu_g(T, p)]}{2}\right) = \sqrt{\frac{p'}{p}} = 0.1\,.$$

The entropy of the adsorbed atoms is equal to

$$S = \frac{\langle E\rangle - F}{T} = k_B\big(\beta\langle E\rangle - \beta\Omega - \langle N\rangle\beta\mu\big)\,,$$

where we divided the Helmholtz free energy $F$ is into the grand potential $\Omega$ and the Gibbs free energy $G = \mu\langle N\rangle$. We already calculated the average energy $\langle E\rangle$ and the average number of the occupied adsorption centers $\langle N\rangle$, whereas the grand potential is obtained by taking the logarithm of the partition function (Problem 12.24). Thus we find that the entropy per adsorption center reads

$$\frac{S(T, p)}{N_0} = k_B\left\{-\frac{\beta[\mu(T, p) + w]}{1 + \exp\big(-\beta[\mu(T, p) + w]\big)} + \ln\Big(1 + \exp\big(\beta[\mu(T, p) + w]\big)\Big)\right\},$$

whereas its change upon the increase of pressure from $p'$ to $p$ is equal to $\Delta S/N_0 = [S(T, p) - S(T, p')]/N_0 \approx 10^{-8}$ eV/K. The entropy is increased in the process; a part of the increase comes from the change of entropy of the atoms that are already adsorbed, whereas the rest originates in the adsorption of additional atoms.

**Problem 12.29.**

*An ideal gas consisting of rod-like molecules is adsorbed at the walls of a container. Upon adsorption, each molecule can attach to the wall in two different ways with the same binding energy. Calculate this energy, given that at* $10^4$ Pa *and* 22 K *the relative occupancy of the adsorption centers is* 1 %*! The kilomolar mass of the gas is* 2 kg/kmol *and the characteristic rotator temperature of the molecules is* 86 K; *the molecules are spinless. What is the relative occupancy of the adsorption centers* *at* 2200 K *if the pressure of the gas and the binding energy of the molecules remain unchanged? The vibrational excitations of the molecules can be neglected.*

The partition function of a system of $N_0$ independent adsorption centers is given by

$$\exp(-\beta\Omega) = \Big[1 + 2\exp\big(\beta(\mu + w)\big)\Big]^{N_0},$$

where $-w < 0$ is the binding energy and $\mu$ is the chemical potential of the adsorbed molecules. The expression with the square brackets is the partition function of a single adsorption center with three possible states: Empty and occupied, the latter in two distinct ways. The average number of adsorbed molecules is

$$\langle N\rangle = -\left(\frac{\mathrm{d}\beta\Omega}{\mathrm{d}\beta\mu}\right)_\beta = \frac{2N_0}{2 + \exp\big(-\beta(\mu + w)\big)}.$$

The above expression can be inverted to express the binding energy

$$w = -\mu - k_B T \ln\left(2\left(\frac{N_0}{\langle N\rangle} - 1\right)\right)$$

in terms of the relative occupancy $\langle N\rangle/N_0$ and $\mu$ which remains to be determined. In equilibrium, $\mu$ must be equal to the chemical potential of the molecular gas obtained by calculating the corresponding partition function using the grand canonical formalism:

$$\begin{aligned}\exp(-\beta\Omega) &= \sum_{N=0}^{\infty} \frac{\exp(\beta\mu N)}{N!\,h^{3N}}\left[\int_V \mathrm{d}\mathbf{r}\left(\int_{-\infty}^{\infty}\exp\left(-\frac{\beta p_x^2}{2m}\right)\mathrm{d}p_x\right)^3 Z_{\mathrm{rot}}\right]^N\\ &= \sum_{N=0}^{\infty}\frac{1}{N!}\left[\frac{\exp(\beta\mu)}{h^3}V\left(\frac{2\pi m}{\beta}\right)^{3/2} Z_{\mathrm{rot}}\right]^N,\end{aligned}$$

where

$$Z_{\mathrm{rot}} = \sum_{j=0}^{\infty}(2j+1)\exp\left(-j(j+1)\frac{T_{\mathrm{rot}}}{T}\right)$$

is the rotational partition function (Problem 11.5), $m$ is the molecular mass, and $T_{\mathrm{rot}}$ is the characteristic rotator temperature. After recalling that $\Omega = -pV$ and $\exp(x) = \sum_{N=0}^{\infty}(x^N/N!)$, one finds that

$$\mu = k_B T \ln\left(\frac{ph^3}{(k_B T)^{5/2}(2\pi m)^{3/2}}\frac{1}{Z_{\mathrm{rot}}}\right).$$

At the temperature of 22 K, which is low compared to $T_{\mathrm{rot}} = 86$ K, virtually no rotational states are excited; hence the gas behaves as if it were monatomic. Thus

$Z_{\mathrm{rot}} \approx 1$ so that $\mu = -14$ meV and $w = 4$ meV. On the other hand, at 2200 K the system is in the high-temperature limit where many rotational states are occupied and thus the discrete sum $Z_{\mathrm{rot}}$ can be approximated by an integral like in a diatomic gas, yielding $Z_{\mathrm{rot}} \approx T/T_{\mathrm{rot}}$. Finally, at this temperature $\mu = -4.2$ eV and $\langle N\rangle/N_0 = 4.8 \times 10^{-10}$.

**Problem 12.30.**
*Upon adsorption from the gaseous phase onto a solid substrate, the argon atoms perform in-plane oscillations around their respective adsorption centers. What is the relative occupancy of the adsorption centers at a temperature of* 140 K *and a gas pressure of* 8 bar *if the binding energy is* 0.1 eV*? Assume that the oscillations of the adsorbed atoms can be described by the Einstein model of uncoupled two-dimensional harmonic oscillators with a frequency of* $5 \times 10^{13}\ \mathrm{s}^{-1}$*! Calculate the average energy of the bound atoms per adsorption center! The kilomolar mass of argon is* 39.9 kg/kmol; *the angular momentum of the atoms is zero.*

The energy of a two-dimensional harmonic oscillator is $E(n_x, n_y) = \hbar\omega(n_x + n_y + 1)$, where $n_x \geq 0$ and $n_y \geq 0$ are the quantum numbers. By adding this energy and the binding energy of $-w$ we obtain the total energy of an adsorbed atom. The grand canonical partition function for $N_0$ independent adsorption centers reads

$$\exp(-\beta\Omega) = \left\{1 + \sum_{n_x=0}^{\infty}\sum_{n_y=0}^{\infty} \exp\Big(\beta\big[\mu + w - \hbar\omega(n_x + n_y + 1)\big]\Big)\right\}^{N_0} .$$

The partition function of a single center (i.e., the expression within the curly brackets) consists of terms corresponding to all possible states of the site—vacant or occupied in any possible oscillator state. Because the oscillations along the two Cartesian axes are independent, the double sum can be factorized to yield

$$\begin{aligned}\exp(-\beta\Omega) &= \Bigg\{1 + \exp\big(\beta(w+\mu)\big) \\ &\qquad \times \left(\sum_{n_x=0}^{\infty} \exp\left[-\beta\hbar\omega\left(n_x + \frac{1}{2}\right)\right]\right)^2\Bigg\}^{N_0} \\ &= \left\{1 + \frac{\exp\big(\beta(w+\mu)\big)}{4\sinh^2(\beta\hbar\omega/2)}\right\}^{N_0} .\end{aligned}$$

The average number of adsorbed atoms is equal to

$$\langle N\rangle = -\left(\frac{\partial\beta\Omega}{\partial\beta\mu}\right)_{\beta} = \frac{N_0}{1 + 4\sinh^2(\beta\hbar\omega/2)\exp(-\beta w) J T^{5/2}/p} ,$$

where $J$ and $p$ stand for the chemical constant of a monatomic gas (see Problem 12.24) and vapor pressure, respectively. Finally $\langle N\rangle/N_0 = 1.55 \times 10^{-3}$.

The average energy of the adsorbed atoms is given by

$$\langle E\rangle = \left(\frac{\partial\beta\Omega}{\partial\beta}\right)_{\beta\mu} = \langle N\rangle\left[\hbar\omega\coth\left(\frac{\beta\hbar\omega}{2}\right) - w\right],$$

where the oscillator term and the binding term are clearly separated. The average energy per adsorption site is $\langle E\rangle = -9.7 \times 10^{-5}$ eV and is negative: The oscillator term is smaller than the binding term so the atoms indeed remain bound.

### Problem 12.31.

*In a simple lattice gas model, each unit cell of a cubic lattice can be either occupied by a particle or empty. Two occupied neighboring cells carry an energy of $-w$ representing an attractive interaction between the particles. Find the critical point of the vapor–liquid coexistence! Hint: Search for the similarities with the Ising model of a ferromagnet and analyze it using the mean-field approximation!*

Each unit cell can be either occupied and empty, hence the analogy with the Ising model where the spin variable $s_i$ can take only one of the two values $\pm 1/2$. By assigning $s_i = +1/2$ to the occupied cells and $s_i = -1/2$ to the empty cells, we can express the number of particles in a given cell by $n_i = s_i + 1/2$. Only pairs of occupied cells contribute to the energy

$$\begin{aligned} E &= -w \sum_{i,j\ \text{neighbors}} n_i n_j \\ &= -w \sum_{i,j\ \text{neighbors}} s_i s_j - \frac{zw}{2}\sum_{i=1}^{N_0} s_i - N_0\frac{zw}{8}, \end{aligned}$$

where $z$ is the coordination number—in a simple-cubic lattice, $z = 6$—and $N_0$ is the number of cells. The total number of particles in the system

$$N = \sum_{i=1}^{N_0}\left(s_i + \frac{1}{2}\right) \le N_0$$

is not fixed in advance, and thus we can apply the grand canonical formalism. The statistical weight in the partition function contains

$$E - \mu N = -w \sum_{i,j\ \text{neighbors}} s_i s_j - \left(\frac{zw}{2} + \mu\right)\sum_{i=1}^{N_0} s_i - N_0\left(\frac{zw}{8} + \frac{\mu}{2}\right),$$

which can be compared with the Ising Hamiltonian (Problem 11.12). In the above expression, the first term is analogous to the exchange interaction between atomic magnetic dipole moments; we notice that in the lattice gas $w$ plays the role of the exchange integral $J$ in the Ising model. The second term is analogous to the coupling with an external magnetic field; from here it follows that $\mu + zw/2$ corresponds to the magnetic flux density. The remaining terms are independent of $s_i$ and thus irrelevant.

The lattice gas model analog of the magnetization $\mathcal{M}$ (and thus of the order parameter) is the particle "density" $N/N_0$. The paramagnetic phase with $\mathcal{M} = 0$ corresponds to a supercritical fluid with an average occupancy of the cells of 1/2. The analogs of the ferromagnetic phases with $\mathcal{M} > 0$ and $\mathcal{M} < 0$ are the liquid and the gas phase; in the former, more than half of the cells are occupied, and in the latter more than half of them are empty. In zero field, the mean-field approximation in the Ising model gives a critical temperature of $zJ/4k_B$ (Problem 11.12). We conclude that the critical temperature of the lattice fluid is

$$T_c = \frac{zw}{4k_B},$$

whereas the critical value of the chemical potential of the two phases is

$$\mu_c = -\frac{zw}{2}.$$

For $\mu > \mu_c$ (i.e., for $\mu + zw/2 > 0$), more than half of the cells are occupied even at $T > T_c$. (In the Ising model this corresponds to matter in a magnetic field where magnetization is nonzero even in the paramagnetic phase.) In this case, a decrease of temperature brings the system from the supercritical fluid state directly to the liquid phase without a phase transition. The opposite is true for $\mu < \mu_c$; in this case, the system continuously transforms into the gas phase. Only for $\mu = \mu_c$ the density of the supercritical fluid is just right such that upon cooling, the system first hits the critical point and then reaches the liquid–gas coexistence.

A number of other problems can be mapped onto the Ising model. One of the examples is the binary mixture of particles $A$ and $B$ with repulsive interactions between the unlike particles. Above the critical temperature, the $A$ and $B$ components are well-mixed, whereas below $T_c$ they phase-separate because of the prevailing repulsive interactions.

# Chapter 13
# Kinetic Theory of Gases

**Problem 13.1.**
*Calculate the average speed of particles in an ideal gas! The velocity is characterized by the Maxwell–Boltzmann distribution.*

The average speed of particles of mass $m_1$ is equal to

$$\langle v \rangle = \int_0^\infty \left(\frac{\beta m_1}{2\pi}\right)^{3/2} \exp\left(-\frac{\beta m_1 v^2}{2}\right) 4\pi v^3 \mathrm{d}v = \sqrt{\frac{8 k_B T}{\pi m_1}} \, .$$

It is instructive to compare it to the speed of sound

$$c = \sqrt{\frac{\kappa k_B T}{m_1}} = \langle v \rangle \sqrt{\frac{\kappa \pi}{8}} \, ,$$

where $\kappa = c_p/c_V$ is the ratio of heat capacities of the gas. Since $\sqrt{\kappa\pi/8} < 1, c < \langle v \rangle$. This result makes sense: A perturbation cannot propagate faster through a medium than its building blocks. At 300 K, the average velocity of molecules in oxygen with $M = 32$ kg/kmol and $\kappa = 1.4$ is $\langle v \rangle = 445$ m/s and the speed of sound is $c = 330$ m/s.

**Problem 13.2.**
*A narrow jet of vaporized silver at* 800 °C *is forced through a horizontal nozzle and hits a screen at a distance of* 5 m. *What is the distribution of the thickness of the silver deposit on the screen? Where is its center of mass? At what point is the deposit thickest?*

We begin by assuming that the mean free path of the atoms in the jet is much larger than the distance between the nozzle and the screen denoted by $l$. In this case, collisions between the atoms can be neglected and since the vapor jet is well-collimated as well as narrow, each atom in the jet can be regarded as a projectile launched in a horizontal direction. The spot on the screen hit by an atom lies $y =$

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$gt^2/2$ below the horizontal line passing through the nozzle; here $g$ is the gravitational acceleration and $t = l/v_x$ is the time of flight. The horizontal component of the velocity $v_x$ remains constant during the flight. For a collimated and narrow jet, we have $v_x \approx v$, where $v$ is the initial velocity. Thus, the silver deposit on the screen is smeared mainly because of spread of the initial velocities of the atoms. The thickness of the deposit in a narrow horizontal strip of width $\mathrm{d}y$ is proportional to the number of particles $\mathrm{d}\phi$ hitting the strip per unit time. Hence, the probability distribution sought is

$$w(y) = \frac{1}{\phi}\left|\frac{\mathrm{d}\phi}{\mathrm{d}y}\right| = \frac{1}{\phi}\left|\frac{\mathrm{d}\phi}{\mathrm{d}v}\frac{\mathrm{d}v}{\mathrm{d}y}\right| = \frac{1}{\phi}\frac{\mathrm{d}\phi}{\mathrm{d}v}\frac{v^3}{gl^2},$$

where $\phi = \int \mathrm{d}\phi$ is the total particle deposition rate. In a vapor of number density $n$, the fraction of atoms moving at a velocity $\mathbf{v}$ is $\mathrm{d}n/n = w(\mathbf{v})\,\mathrm{d}\mathbf{v} = w(\mathbf{v})v^2\,\mathrm{d}v\,\Delta\Omega$, where $\Delta\Omega$ is the solid angle of the jet and $v = |\mathbf{v}|$. Thus $\mathrm{d}\phi = nv_x w(\mathbf{v})v^2\,\mathrm{d}v\,A\Delta\Omega$, $A$ being the surface area of the cross section of the nozzle. The velocity distribution $w(\mathbf{v})$ is Maxwellian:

$$w(v) = \left(\frac{\beta m_1}{2\pi}\right)^{3/2}\exp\left(-\frac{\beta m_1 v^2}{2}\right),$$

where $m_1 = M/N_A$ is the mass of a single atom; $M = 107.9$ kg/kmol. Since $v_x \approx v$ we have $\mathrm{d}\phi = nw(v)v^3\,\mathrm{d}v\,A\Delta\Omega$. Hence the number rate of atoms hitting the screen is given by

$$\phi = n\,A\Delta\Omega\int_0^\infty w(v)v^3\,\mathrm{d}v = \frac{n\,A\Delta\Omega}{\sqrt{2\beta m_1\pi^3}},$$

whereas the probability distribution of the atom deposition coordinate $y$ (which is proportional to the local thickness of the deposit) reads

$$w(y) = \frac{(\beta m_1 gl^2)^2}{16y^3}\exp\left(-\frac{\beta m_1 gl^2}{4y}\right)$$

(Figure 13.1). The center of mass of the deposit is located at

$$\langle y\rangle = \int_0^\infty w(y)y\,\mathrm{d}y = \frac{\beta m_1 gl^2}{4} = 0.744\ \mathrm{mm}$$

below the horizontal line through the nozzle. The locus of the thickest deposit is determined by $\mathrm{d}w(y)/\mathrm{d}y = 0$ and is at

$$y_0 = \frac{\beta m_1 gl^2}{12} = 0.248\ \mathrm{mm}.$$

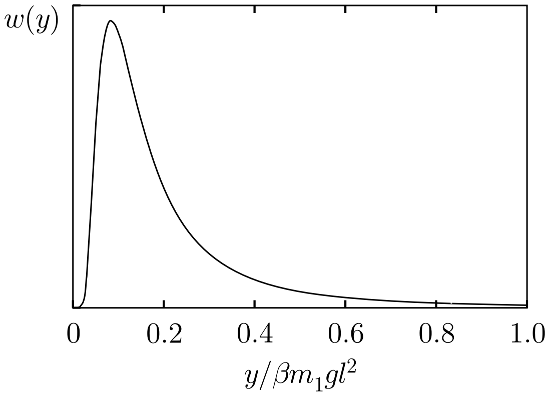

**Fig. 13.1** Probability distribution $w(y)$ is proportional to the thickness of the silver deposit. If an atom was to hit the screen at $y = 0$, its velocity should be infinite; thus $w(0) = 0$. On the other hand, the atoms hitting the screen at $y \to \infty$ must be very slow and since their number is small, $w(y \to \infty)$ approaches 0 too

## Problem 13.3.

*The flux of thermal neutrons in the core of a nuclear reactor is* $4 \times 10^{16}\,\mathrm{m}^{-2}\mathrm{s}^{-1}$. *What is the number density of the neutrons? What is their partial pressure? The distribution of velocities is Maxwellian at a temperature of* 300 K.

We consider neutrons with a velocity component along the $x$ axis equal to $v_x$ that pass through an imaginary frame of area $A$ oriented perpendicular to the $x$ axis. (In the same manner one can estimate, e.g., the maximum rate of evaporation or condensation at a liquid–vapor interface, or the flux of a rarefied gas escaping from a vessel into vacuum.) Within a time interval $\Delta t$, all neutrons located within a cuboid of a base of surface area of $A$ and a height of $v_x\,\Delta t$ adjacent to the frame will pass through the frame (Fig. 13.2). The number of these neutrons is $nAv_x\,\Delta t$, where $n$ is the number density. Now recall that the neutron velocities are distributed rather than fixed; thus the total number of neutrons traveling through the frame along the $x$ axis is given by

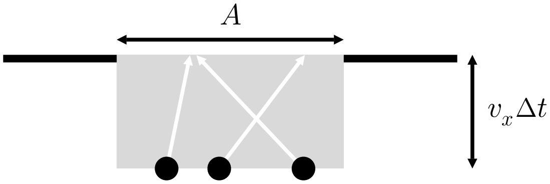

**Fig. 13.2** Flux of particles through a frame of surface area $A$: The number of particles with a normal velocity component $v_x$ that pass through the frame in a time interval $\Delta t$ is equal to the number of particles within the shaded region. The white arrows are the paths of three selected particles that are among the last ones to cross the frame

$$N = \int_0^\infty nAv_x w(v_x)\,\mathrm{d}v_x\,\Delta t = jA\,\Delta t\,,$$

where $j$ is the flux of the neutrons and

$$w(v_x) = \left(\frac{\beta m_1}{2\pi}\right)^{1/2} \exp\left(-\frac{\beta m_1 v_x^2}{2}\right)$$

is the distribution of the component of the velocity along the $x$ axis $v_x$. The flux of neutrons with $v_x > 0$ through the frame is counterbalanced by the flux in the opposite direction with $v_x < 0$; as they are equal on average, the net macroscopic flux vanishes. The flux defined above pertains only to the flow through the frame in one direction—as if the neutrons effused through a hole in a vessel into vacuum. Therefore the above integral goes only over $v_x > 0$ and we have

$$j = \frac{n}{\sqrt{2\pi\beta m_1}} = \frac{n\langle v\rangle}{4}\,,$$

where $j$ is expressed in terms of average speed $\langle v\rangle = (8/\pi\beta m_1)^{1/2}$ (Problem 13.1). The numerical results are $\langle v\rangle = 2510$ m/s and $n = 6.37 \times 10^{13}$ m$^{-3}$.

Alternatively, the expression for the flux of the particles can be derived in spherical coordinates where the polar angle $\theta$ is measured with respect to the $x$ axis and the integral over the direction of the velocity is carried out only over one hemisphere of the velocity space. In this case, the number of neutrons at a velocity $v$ passing through the frame during a time interval of $\Delta t$ is equal to $nAv\cos\theta\,\Delta t$. By integrating over the magnitude of the velocity and all allowed directions, we obtain

$$N = \int_0^\infty nw(v)v^3\mathrm{d}v \int_\Omega A\,\Delta t\cos\theta\,2\pi\sin\theta\,\mathrm{d}\theta = jA\,\Delta t\,,$$

so that

$$\begin{aligned} j &= n\left(\frac{\beta m_1}{2\pi}\right)^{3/2} \int_0^\infty \exp\left(-\frac{\beta m_1 v^2}{2}\right) v^3\,\mathrm{d}v \int_0^{\pi/2} 2\pi\cos\theta\sin\theta\,\mathrm{d}\theta \\ &= \frac{n\langle v\rangle}{4}\,. \end{aligned}$$

When calculating the pressure, we consider the collisions of the neutrons with the wall and we estimate the impulse of the force $\mathcal{F}_x$ exerted by the neutrons in the direction perpendicular to the wall. Upon each collision, the normal component of the linear momentum of a neutron changes by $2m_1v_x$. During a time interval of $\Delta t$, a wall of surface area $A$ is hit by $nAv_x\,\Delta t$ neutrons with a normal velocity component of $v_x$. Thus, the combined change of the linear momenta of all neutrons with $v_x > 0$ reads

$$\int_0^\infty 2m_1 nAv_x^2 w(v_x)\,\mathrm{d}v_x\,\Delta t = \mathcal{F}_x\,\Delta t,$$

and is equal to the impulse of the force. The pressure reads

$$p = \frac{\mathcal{F}_x}{A} = m_1 n \int_{-\infty}^{\infty} v_x^2 w(v_x)\,\mathrm{d}v_x = nm_1\langle v_x^2\rangle = nk_BT\,.$$

In the last step, we used the equipartition theorem $m_1\langle v_x^2\rangle/2 = k_BT/2$ and we obtained the ideal gas law. This is not surprising: We neglected the interactions between neutrons and the origin of the pressure is entirely kinetic. The numerical result for the pressure is $p = 2.64 \times 10^{-7}$ Pa.

**Problem 13.4.**
*A spherical vessel of a volume of* $10\,\mathrm{dm}^3$ *contains water vapor at* $20\,^\circ\mathrm{C}$ *and* 10 mbar. *At some point, a small patch of the wall is cooled so that all molecules that hit it remain trapped at the wall. What is the surface area of the cooled patch of the wall if the vapor pressure is to drop to* 0.1% *of its initial value within one second? The vapor temperature is kept constant. The kilomolar mass of water is* 18 kg/kmol.

The cold patch of the wall behaves like a hypothetical opening which allows the water molecules to escape from the vessel into vacuum. The molecular flux through the opening is equal to $j = n\langle v\rangle/4$, where $n$ is the number density of the molecules, $\langle v\rangle = \sqrt{8k_BT/\pi m_1}$ is their average speed, and $m_1 = M/N_A$ is the mass of a single molecule. During a time interval $\mathrm{d}t$ the number of free molecules inside the vessel $N$ decreases by

$$\mathrm{d}N = -jA_0\,\mathrm{d}t = -\frac{1}{4}n\langle v\rangle A_0\,\mathrm{d}t\,,$$

where $A_0$ denotes the surface area of the cold patch. The pressure within the vessel is described by the ideal gas law $p = nk_BT$, where $n = N/V$ and $V$ is the vessel volume. By expressing $\mathrm{d}N$ and $n$ in terms of $p$ we obtain

$$\frac{\mathrm{d}p}{p} = -\frac{\langle v\rangle A_0}{4V}\,\mathrm{d}t\,.$$

Now we integrate the left-hand side of this result over pressure from $p'$ to $p$ and the right-hand side over time:

$$\ln\left(\frac{p'}{p}\right) = \frac{\langle v\rangle A_0 t}{4V}\,.$$

The pressure decreases exponentially with time. To invoke a pressure decrease to one per mill of the initial value within 1 s, the surface area of the cold patch must be equal to

$$A_0 = \frac{4V}{\langle v\rangle t}\ln\left(\frac{p'}{p}\right) = 4.7\ \mathrm{cm}^2$$

The total surface area of the vessel can be deduced from its volume: Its radius is equal to $R = (3V/4\pi)^{1/3} = 13.4$ cm and the surface is $A = 4\pi R^2 = 0.224\ \mathrm{m}^2$. Thus the cold patch is just a small fraction of total surface area since $A_0/A = 2.1 \times 10^{-3}$. This provides *a posteriori* justification of our ignoring the curvature of the wall.

**Problem 13.5.**

*A one-liter container with a mass of only* 10 g *located in the outer space is filled with helium at a temperature of* 100 K *and a pressure of* 10 Pa. *The container has a small hole with an area of* $0.01\ \mathrm{mm}^2$, *which is initially closed. At some point, the hole is carefully opened by an astronaut and the container begins to move. Calculate the speed of the container with respect to the astronaut* 1 *minute after the hole is opened! What is the highest speed of the container? The container is equipped with a tiny heater that maintains the temperature of the gas constant. The kilomolar mass of helium is* 4 kg/kmol.

The container accelerates because of the reaction force equal to $\mathcal{F} = pA$, where $A$ is the area of the hole and $p = nk_BT$ is the pressure of the gas. The acceleration is expected to be small; therefore we can neglect the inhomogeneities of the gas due to acceleration. Furthermore, the mass of the gas can be neglected with respect to the proper mass of the container $m$. In the coordinate system of the astronaut (which approximately coincides with the inertial center-of-mass system), the equation of motion reads

$$m\,\mathrm{d}u = \mathcal{F}\,\mathrm{d}t = n(t)k_BTA\,\mathrm{d}t\,,$$

where $u$ is the velocity of the container with respect to the astronaut and $n(t)$ the number density of gas in the container. In a time interval $\mathrm{d}t$, $\mathrm{d}N = V\,\mathrm{d}n$ helium atoms escape from the container ($V$ being its volume) so that $\mathrm{d}N = -jA\,\mathrm{d}t = -(n\langle v\rangle/4)A\,\mathrm{d}t$; $\langle v\rangle$ is the average speed of the atoms (Problem 13.1). Like in Problem 13.4 we realize that

$$n(t) = \frac{p'}{k_BT}\exp\left(-\frac{\langle v\rangle At}{4V}\right),$$

where $p'$ is the initial pressure of the gas, and the equation of motion can be recast as

$$u(t) = \frac{p'A}{m}\int_0^t \exp\left(-\frac{\langle v\rangle At}{4V}\right)\mathrm{d}t = \frac{4p'V}{m\langle v\rangle}\left[1 - \exp\left(-\frac{\langle v\rangle At}{4V}\right)\right].$$

A minute after the hole is opened, the velocity of the container is 0.57 mm/s; after a long time it approaches 5.5 mm/s. We inserted $\langle v\rangle = (8k_BTN_A/\pi M)^{1/2} = 726$ m/s.

We now estimate the mean free path of the helium atoms in the container:

$$\langle l_f\rangle = \frac{1}{4\pi r_1^2 n} \gtrsim \frac{k_BT}{4\pi r_1^2 p'} \approx 1.1\ \mathrm{mm}\,.$$

Here we estimated the atom size by $r_1 \approx 10^{-10}$ m. The mean free path exceeds the diameter of the hole $\sim \sqrt{A} = 0.1$ mm. This means that the flow through the hole is not macroscopic and that the interatomic collisions can be neglected.

**Problem 13.6.**
*A thermostat contains a vessel of a volume of* 2 l *divided by a wall into two identical chambers. In the wall there is a hole, that is sealed at the beginning. Initially one chamber is evacuated, whereas the other one contains air at a pressure of* $10^{-3}$ mbar. *How long does it take for the pressures in the two parts to become approximately equal? The temperature is* 300 K *and the cross-sectional area of the hole is* 0.01 mm$^2$.

Since the density of the gas is low, the mean free path is much larger than the hole diameter $\sim \sqrt{A}$ and hence there is no macroscopic flow through the hole. For the number of molecules in chamber 1 we have $\mathrm{d}N_1/\mathrm{d}t = -Aj_{1\to 2} + Aj_{2\to 1}$, where $j_{1\to 2} = n_1\langle v\rangle/4$ is the particle flux from chamber 1 to chamber 2, and $j_{2\to 1} = n_2\langle v\rangle/4$ the corresponding flux in the opposite direction. At any time, the total number of molecules has to be equal to the initial number of molecules in chamber 1, $N_1(t) + N_2(t) = N$ so that $n_1(t) + n_2(t) = N/V$; here $V$ is the volume of either chamber. Therefore

$$\frac{\mathrm{d}n_1}{\mathrm{d}t} = -\frac{A\langle v\rangle}{2V}n_1 + \frac{A\langle v\rangle N}{4V^2}\,.$$

The solution of this differential equation is $n_1(t) = C_1\exp(-t/\tau) + C_2$, where $\tau = 2V/A\langle v\rangle$. The initial condition is $n_1(0) = N/V$ and after a long time, one must have $n_1 = n/2V$ so that $C_1 = C_2 = N/2V$. Hence

$$n_1(t) = \frac{N}{2V}\left[1 + \exp\left(-\frac{t}{\tau}\right)\right],$$

and since $n_1(t) + n_2(t) = N/V$

$$n_2(t) = \frac{N}{2V}\left[1 - \exp\left(-\frac{t}{\tau}\right)\right].$$

Strictly speaking, the pressures never equalize, but there still exists a well-defined relaxation time of pressure relaxation given by $\tau = 2V/A\langle v\rangle = 428$ s. After $3\tau \approx 21$ min the chamber pressures differ from their final equilibrium values by less than 5%.

**Problem 13.7.**
*A vessel contains a* 1 : 1 *mass-ratio mixture of hydrogen and helium at* 0.01 mbar *and* 20 °C. *A small hole is drilled into the wall of the vessel to let the mixture leak into an adjacent chamber where a high vacuum is maintained by pumping. What is the helium concentration in this chamber?*

The pressure of the gas in the chamber is small; therefore, the reverse chamber-to-vessel gas flux can be neglected. In this case, the ratio of the number densities of the helium atoms and hydrogen molecules ($n_1$ and $n_2$, respectively) is equal to the ratio of the corresponding fluxes: $n_1/n_2 = j_1/j_2$. The fluxes, in turn, depend on the particle number densities inside the vessel $n_i'$ as well as on the corresponding average particle speed and read $j_i = n_i'\langle v_i\rangle/4$. Here $\langle v_i\rangle = \sqrt{8k_BT/\pi m_i}$, where $m_i$ is the mass of either hydrogen molecule or helium atom. Hence

$$\frac{n_1}{n_2} = \frac{n_1'}{n_2'}\sqrt{\frac{m_2}{m_1}} = \frac{1}{2\sqrt{2}},$$

where we took into account that since $m_1 = 2m_2$, equal mass fractions of helium and hydrogen in the vessel correspond to $n_1'/n_2' = 0.5$. Hence, the mass fraction ratio of the two components of the mixture inside the chamber is twice the ratio $n_1/n_2$, i.e., $1/\sqrt{2}$, and the helium concentration is

$$x_1 = \frac{m_1/m_2}{1 + m_1/m_2} = 0.414\,.$$

A similar procedure is used in isotope separation.

**Problem 13.8.**

*A vessel filled with rarefied oxygen is divided into two chambers by a porous wall. In the left and the right chamber, constant temperatures of* 27 °C *and* 30 °C *are maintained, respectively. What is the pressure difference between the chambers if the pressure in the left one is* 10 Pa*? What happens if the chambers are additionally connected by a thick tube? Calculate the particle flow rate through the tube if the total cross section of all pores is* $10^{-4}$ m$^2$*!*

The vessel with a porous wall is depicted in Fig. 13.3. We denote the pressure and the temperature in the left chamber by $p_1$ and $T_1$, respectively, whereas those in the right chamber are $p_2$ and $T_2$. The diameter of the pores is much smaller than the mean free path of the oxygen molecules. In the stationary state, the particle fluxes between the chambers are equal so that $n_1\langle v\rangle_1/4 = n_2\langle v\rangle_2/4$. Due to the different temperatures in the chambers, the average molecular speeds $\langle v\rangle_{1,2} = \sqrt{8k_BT_{1,2}/\pi m_1}$ (here $m_1$ is the mass of the oxygen molecule) are different too and so are the number densities of the gases $n_{1,2} = p_{1,2}/k_BT_{1,2}$. Thus

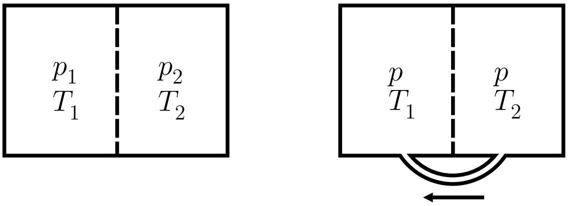

**Fig. 13.3** Vessel with a porous internal wall without (left) and with a thick connecting tube (right)

$$\frac{p_1}{p_2} = \sqrt{\frac{T_1}{T_2}} \approx 0.995\,.$$

The pressure difference $p_2 - p_1$ is equal to 0.05 Pa. The phenomenon where a temperature difference induces a difference in pressure is referred to as the thermomechanical effect.

If the chambers are connected by an additional tube of a diameter much larger than the mean free path, the initial pressure difference causes a net macroscopic gas flow through the tube. This flow does not cease even after a mechanical equilibrium is established and the pressures $p_1$ and $p_2$ are equal because the flow through the porous wall is inversely proportional to $\sqrt{T}$. As a result, the flow from the hot to the cold chamber is smaller than in the opposite direction. (Phenomenologically, this effect is similar to the thermoelectric effect where a temperature difference induces a stationary electric current.) At a pressure of $p = 10$ Pa, the total particle flow rate through the wall (and through the tube in the opposite direction) is equal to

$$\phi = \frac{pA}{\sqrt{2\pi m_1 k_B}}\left(\frac{1}{\sqrt{T_1}} - \frac{1}{\sqrt{T_2}}\right) = 1.33 \times 10^{17}\ \mathrm{s}^{-1}\,,$$

where $A$ is the total cross section of all pores.

**Problem 13.9.**

*A nondegenerate two-dimensional electron gas is subjected to an external potential given by* $\phi(x, y) = c_2(x^2 + y^2) - c_4(x^2 + y^2)^2$*. In thermal equilibrium at* $5 \times 10^3$ K, *most of the electrons are trapped inside the potential well but some of them manage to escape. Estimate the escape probability per unit time! Use* $c_2 = 10^{-2}\ \mathrm{eV/nm}^2$ and $c_4 = 10^{-6}\ \mathrm{eV/nm}^4$*!*

Because of the rotational symmetry of the potential shown in Fig. 13.4, we write the potential as $\phi(r) = c_2 r^2 - c_4 r^4$, where $r = \sqrt{x^2 + y^2}$. The maximum of the

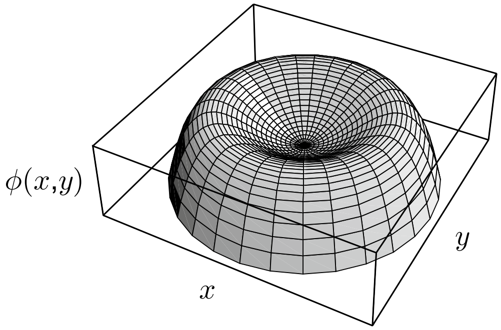

**Fig. 13.4** Sketch of the potential $\phi(x, y)$: The origin of the coordinate system is at the bottom of the well; only electrons that are fast enough can escape

potential corresponds to $\mathrm{d}\phi(r)/\mathrm{d}r = 0$ and is located at $r_0 = (c_2/2c_4)^{1/2}$. Only electrons that are sufficiently fast can escape across the maximum. In a time interval $\mathrm{d}t$, a total of $2\pi r_0 n_A v_r \,\mathrm{d}t$ electrons with a radial velocity component $v_r > 0$ can escape ($n_A$ denotes the local electron density per unit surface), the total escape rate being

$$\frac{\mathrm{d}N}{\mathrm{d}t} = 2\pi r_0 n_A(r_0) \int_0^\infty w(v_r) v_r \,\mathrm{d}v_r = r_0 n_A(r_0) \sqrt{\frac{2\pi}{\beta m_1}} \,.$$

Here $w(v_r) = (\beta m_1/2\pi)^{1/2} \exp(-\beta m_1 v_r^2/2)$; $m_1$ stands for the mass of electron. The velocity distribution is Maxwellian regardless of the external potential, but the electron density $n_A(r) = n_A(0) \exp\left(-\beta\phi(r)\right)$ depends on position. To estimate $\mathrm{d}N/\mathrm{d}t$, one must find the density of the electrons at the maximum of the potential $n_A(r_0)$ which depends on the total number of electrons $N = \int_0^\infty n_A(r)\, 2\pi r \,\mathrm{d}r$. As the electrons are mostly located in the potential well close to the origin, $\exp\left(-\beta\phi(r)\right)$ can be expanded:

$$\exp\left(-\beta\left(c_2 r^2 - c_4 r^4\right)\right) \approx \left(1 + \beta c_4 r^4\right) \exp\left(-\beta c_2 r^2\right) .$$

By integrating by parts we obtain

$$N = \frac{\pi n_A(0)}{\beta c_2} \left(1 + \frac{2c_4}{\beta c_2^2}\right)$$

and

$$n_A(r_0) = \frac{N \beta c_2}{\pi\left(1 + 2c_4/\beta c_2^2\right)} \exp\left(-\frac{\beta c_2^2}{4c_4}\right) .$$

Thus the escape probability per unit time is given by

$$\frac{1}{N}\frac{\mathrm{d}N}{\mathrm{d}t} \approx \sqrt{\frac{\beta c_2^3}{\pi m_1 c_4}} \exp\left(-\frac{\beta c_2^2}{4c_4}\right) = 2.4 \times 10^{-11}\ \mathrm{s}^{-1} .$$

At the end, we took into account that $2c_4/\beta c_2^2 \ll 1$.

### Problem 13.10.

*The surface area of the mantle of a Dewar flask is* 5 dm$^2$. *The walls of the mantle are separated by a* 3 mm-*thick gap filled by air at* $10^{-3}$ mbar. *The flask contains ice at* 0 °C, *whereas the outside temperature is* 20 °C. *Estimate the mass of ice that melts in one hour! What is the result if the air pressure is increased* $10^4$ *times? Estimate the mean free path of the molecules in the two cases! The kilomolar mass of air is* 29 kg/kmol.

We first calculate the molecular mean free path in the layer of air at $10^{-3}$ mbar:

$$\langle l_f \rangle = \frac{k_B T}{4\pi r_1^2 p} \approx 7.5\ \mathrm{cm} ,$$

where we approximated the radius of the molecules by $r_1 \approx 0.2$ nm and we inserted $T = 0\,^\circ\mathrm{C}$. Since the mean free path is significantly larger than the width of the gap between walls of the mantle, the intermolecular collisions in the layer are rare and thus there exists no continuous temperature profile. We further assume perfect accommodation of each molecule when it hits any of the two walls such that the molecule is thermalized to the temperature of the wall. Under such circumstances the heat flux carried from the wall by the molecules is given by

$$j_Q = n \int_0^\infty w(v)E(v)v^3\,\mathrm{d}v \int_0^{\pi/2} 2\pi\cos\theta\sin\theta\,\mathrm{d}\theta\,;$$

the angle $\theta$ is measured with respect to to the normal of the wall. The above expression is analogous to that used in the derivation of the pressure exerted on a wall (Problem 13.3), except that the transmitted linear momentum is replaced by the transmitted energy $E(v)$. In a monatomic gas, this energy consists of the translational kinetic energy $E(v) = m_1v^2/2$, and thus

$$\begin{aligned} j_Q &= \left(\frac{\beta m_1}{2\pi}\right)^{3/2} \frac{nm_1}{2} \int_0^\infty \exp\left(-\frac{\beta m_1 v^2}{2}\right) v^5\,\mathrm{d}v \\ &\quad\times \int_0^{\pi/2} 2\pi\cos\theta\sin\theta\,\mathrm{d}\theta \\ &= nk_BT\sqrt{\frac{2k_BT}{m_1\pi}} = \frac{n\langle v\rangle}{2}k_BT\,, \end{aligned}$$

where the result is expressed using the average speed $\langle v\rangle$ and $m_1 = M/N_A$. An alternative (but approximate) approach would be to estimate $j_Q$ by multiplying the particle flux $j = n\langle v\rangle/4$ by $3k_BT/2$ (borrowed from the equipartition theorem). The functional dependence of the thus derived $j_Q$ on temperature and density is correct but the numerical prefactor is wrong because of $\langle v\rangle\langle v^2\rangle \neq \langle v^3\rangle$.

However, air is a diatomic gas and its internal energy is due to both translational and rotational motion. Therefore, we have $E(v) = m_1v^2/2 + E_r$, where $E_r$ is the rotational energy which is independent of the translational motion. For this reason, the rotational contribution to $j_Q$ is simply given by $(n\langle v\rangle/4)\langle E_r\rangle$. As a diatomic molecule has two rotational degrees of freedom, the equipartition theorem gives $\langle E_r\rangle = k_BT$ and the total heat flux from the wall is equal to

$$j_Q = \frac{n\langle v\rangle}{2}k_BT + \frac{n\langle v\rangle}{4}\langle E_r\rangle = \frac{3n\langle v\rangle}{4}k_BT = \frac{3p\langle v\rangle}{4}\,.$$

Here we used the ideal gas law.

In the stationary state, the number fluxes of the molecules from wall to wall in the flask mantle are equal, and so a given $n\langle v\rangle/4$ implies $j_Q \propto T$. Hence the heat flux from the hot wall to the cold one is larger than that in the opposite direction. The difference of the fluxes

$$\Delta j_Q = j_Q(T + \Delta T) - j_Q(T) = \frac{3n\langle v\rangle}{4} k_B \Delta T = 2.4\,\mathrm{W/m^2}$$

is warming up the contents of the flask. It is proportional to the density of the gas and to the temperature difference of the walls but it does not depend of the width of the gap between the walls. (When calculating $\langle v\rangle = \sqrt{8k_B T/\pi m_1}$ and $n = p/k_B T$ we used the mean temperature of $10\,^\circ\mathrm{C}$ and we obtained $\langle v\rangle = 454$ m/s and $n = 2.56 \times 10^{19}/\mathrm{m}^3$.) The mass of ice that melts in 1 hour is

$$\frac{\Delta j_Q A t}{q_f} = 1.3\ \mathrm{g}\,;$$

here $A$ is the surface area of the walls of the flask and $q_f$ is the heat of fusion.

If the air pressure is increased by a factor of $10^4$, the mean free path becomes $10^4$ times shorter and is equal to $\langle l_f\rangle \approx 7.5\ \mu\mathrm{m}$, which is much less than the width of the gap between the walls. The intermolecular collisions are now frequent enough and an equilibrium temperature profile $T(z)$ is established in the layer of air, the temperature being a linear function of the distance from a reference wall $z$. The heat flux emitted by the hot wall still exceeds that emitted by the cold wall but now we can assume that at a given $z$, molecules with an average energy of $5k_B T(z)/2$ originate at a location where they last collided with another molecule, that is at $z \pm \langle l_f\rangle$:

$$\begin{aligned}\Delta j_Q &= j_Q(T + \Delta T) - j_Q(T - \Delta T)\\ &= \frac{n\langle v\rangle}{4}\left[\frac{5k_B}{2}\left(T + \frac{\mathrm{d}T}{\mathrm{d}z}\langle l_f\rangle\right) - \frac{5k_B}{2}\left(T - \frac{\mathrm{d}T}{\mathrm{d}z}\langle l_f\rangle\right)\right]\\ &= \frac{5\langle v\rangle k_B}{16\pi r_1^2}\frac{\mathrm{d}T}{\mathrm{d}z} = 104\,\mathrm{W/m^2}\,.\end{aligned}$$

When we evaluated $\langle v\rangle$, we again inserted the mean temperature. The resulting total heat flux is proportional to the temperature difference between the walls and inversely proportional to the wall-to-wall distance but independent of the density of the gas. At the larger pressure, 56 g of ice melt in 1 hour, which is much more than at $10^{-3}$ mbar.

## Problem 13.11.

*A one-liter thermally insulated vessel contains oxygen at* $27\,^\circ\mathrm{C}$ *and* 0.01 mbar. *The vessel is equipped with a valve of a diameter of* 0.1 mm *which is opened. How long does it take for the oxygen temperature to drop to a half of the initial value? The vessel is placed in vacuum. What is the temperature of the oxygen in the vessel after half of it has escaped?*

The diameter of the valve is much smaller than the mean free path of the oxygen molecules; therefore, there is no macroscopic flow of molecules leaving the vessel. The temperature of the gas decreases with time because on average, the molecules that manage to escape are faster and carry more energy than those that remain in the vessel. The change of the internal energy is given by $c_V\,\mathrm{d}(mT)$, where $m$ and $T$ stand for the instantaneous mass and temperature of the gas inside the vessel, respectively, and $c_V$ is the heat capacity at constant volume. The internal energy changes both because of the temperature decrease and because of the mass loss. The expression for the energy flow rate escaping the vessel is borrowed from Problem 13.10. The first law of thermodynamics for the gas remaining in the vessel reads

$$c_V\,\mathrm{d}(mT) = -\frac{3}{4}n\langle v\rangle k_B T A\,\mathrm{d}t\,,$$

where $A$ is the surface area of the valve. We write $m = nVM/N_A$, where $V$ is the vessel volume and $n$ is the instantaneous number density of the gas, and we take into account that $c_V = 5k_BN_A/2M$. After some reaarangements, the left-hand side reduces to $\mathrm{d}(nT) = n\,\mathrm{d}T + T\,\mathrm{d}n$ where $\mathrm{d}n = -(n\langle v\rangle/4V)A\,\mathrm{d}t$ like in Problem 13.4. We are left with

$$\mathrm{d}T = -\frac{\langle v\rangle AT}{20V}\,\mathrm{d}t\,.$$

Recall that the average speed of the oxygen molecules depends on the temperature: $\langle v\rangle = \sqrt{8k_BT/\pi m_1}$, where $m_1 = M/N_A$ is the mass of the molecule. Finally

$$\int_{T'}^{T'/2}\frac{\mathrm{d}T}{T^{3/2}} = -\frac{A}{10V}\sqrt{\frac{2k_B}{\pi m_1}}\int_0^t \mathrm{d}t\,.$$

After integration, we find that the temperature drops to a half of the initial value $T'$ after a time of

$$t = 20\left(\sqrt{2}-1\right)\frac{V}{A}\sqrt{\frac{\pi m_1}{2k_BT'}} = 1.32\ \mathrm{h}\,.$$

To calculate the temperature after half of the gas has escaped, the heat flux $j_Q$ must be expressed in terms of the particle flux $j$ which, in turn, can be related to the mass flux $j_m$: $j_Q = 3k_BTj$ and $j = j_m/m_1 = -(m_1A)^{-1}\mathrm{d}m/\mathrm{d}t$. These two results are now inserted into the above form of the first law to yield

$$\frac{\mathrm{d}T}{T} = \frac{1}{5}\frac{\mathrm{d}m}{m}.$$

After half of the gas has escaped, the temperature of the gas in the vessel is equal to $2^{-1/5}T' = 0.870\,T' = 261$ K. The above expression represents the equation of an (irreversible) adiabatic process. Note that it differs from the reversible adiabatic relation $\mathrm{d}T/T = (2/5)\,\mathrm{d}m/m$ which follows from the equation of state and the first law of thermodynamics for a diatomic ideal gas escaping from a vessel through a large hole. The two relations disagree because the latter holds in cases where a macroscopic flow from a vessel can be observed, which does not apply here because the valve is too small.

**Problem 13.12.**
*Calculate the Doppler broadening of a spectral line emitted by rarefied helium at* 501.6 nm*! The temperature is* 300 K. *Compare the result with the broadening due to collisions between atoms at the same temperature and* 1 bar*! The radius of the helium atom is* 0.122 nm.

We consider a spectral line at a frequency of $\nu_0$; the natural line width can be neglected compared to the two types of broadening of interest. The motion of atoms in a gas leads to the Doppler effect upon emission of light: The atoms that move away from the observer emit at a frequency lower than $\nu_0$ and those moving toward the observer emit at a frequency higher than $\nu_0$. If the component of the velocity in the direction of observation $v_x$ is much smaller than the speed of light $c$, the measured frequency is given by $\nu(v_x) = \nu_0(1 + v_x/c)$. This implies that

$$v_x = c\left(\frac{\nu}{\nu_0} - 1\right).$$

The frequency distribution $w_\nu(\nu)$ is deduced from the probability distribution over the component of the velocity along the $x$ axis denoted by $w(v_x)$

$$w_\nu(\nu) = w(v_x)\frac{\mathrm{d}v_x}{\mathrm{d}\nu} = \frac{c}{\nu_0}\left(\frac{\beta m_1}{2\pi}\right)^{1/2} \exp\left(-\frac{\beta m_1 c^2(\nu - \nu_0)^2}{2\nu_0^2}\right).$$

The Doppler line width can now be extracted from the argument of the exponential function above and is given by

$$\Delta\nu_D \approx \nu_0\sqrt{\frac{2k_BT}{m_1c^2}} = 2.22 \times 10^9 \text{ s}^{-1}.$$

Here, $\nu_0 = c/\lambda_0$ with $\lambda_0 = 501.6$ nm and $m_1 = M/N_A$ with $M = 4$ kg/kmol. Hence, the corresponding relative line width is equal to $\Delta\nu_D/\nu_0 \approx 3.71 \times 10^{-6}$, which is roughly 100 times larger than the natural line width.

The undisturbed emission of light by an atom takes place only between consecutive collisions with other atoms, which also results in a spectral line broadening. The time between two collisions is estimated as the ratio of mean free path and average velocity:

$$\tau = \frac{\langle l_f\rangle}{\langle v\rangle} = \frac{1}{4r_1^2p}\sqrt{\frac{k_BTm_1}{8\pi}} = 1.76 \times 10^{-10} \text{ s},$$

where $r_1$ is the atomic radius and $p$ is the pressure of the gas. The line width due to collisions $\Delta\nu_T$ is estimated from the relation

$$\Delta\nu_T \sim (2\pi\tau)^{-1} = 9.06 \times 10^8 \text{ s}^{-1}.$$

The corresponding relative width is $\Delta\nu_T/\nu_0 \approx 9.08 \times 10^{-7}$. Thus the Doppler broadening is dominant in the spectrum of helium.

**Problem 13.13.**
*A* 3 mm-*thick layer of air at* $0\,^\circ\mathrm{C}$ *and* $10^{-3}$ mbar *is confined between two large parallel plates. What is the shear stress when the plates move in opposite directions with relative velocity* 1 cm/s *at a constant separation? How does the result change when the air pressure is increased* $10^4$ *times? The kilomolar mass of air is* 29 kg/kmol.

The mean free path at $0\,^\circ\mathrm{C}$ and $10^{-3}$ mbar is about 7.5 cm, which is much more than the distance between the plates. In this case, the intermolecular collisions are not frequent enough to establish an equilibrium velocity profile between the plates. The shear stress—the flux of linear momentum—is thus obtained by considering the molecular collisions with the moving plates: The molecules originating from the first plate slow down the second plate and vice versa. We assume perfect accommodation, which means that the average tangential velocity component of the rebounding molecules is identical to the velocity of the plate that they hit. In time $\Delta t$ a patch of size $A$ of the plate is hit by $jA\Delta t$ molecules, where $j = n\langle v\rangle/4$ is the average molecular flux (Problem 13.3). Each molecule carries a momentum $m_1 u$ from plate to plate, where $m_1$ is the mass of a single molecule and $u$ is the relative velocity of the plates. All collisions result in an impulse of the force of $\mathcal{F}\Delta t = jAm_1u\Delta t$ so that the shear stress is

$$\frac{\mathcal{F}}{A} = \frac{\rho\langle v\rangle u}{4} = \frac{pM}{4RT}\langle v\rangle u = \frac{pu\sqrt{M}}{\sqrt{2\pi N_A k_B T}}\,.$$

Here we expressed the number density $n$ in terms of the density $\rho = nm_1$, which is related to pressure by the ideal gas law $\rho = pM/RT$; we also inserted the expression for $\langle v\rangle$. The final numerical result is $\mathcal{F}/A = 1.43 \times 10^{-6}\ \mathrm{N/m^2}$. Like heat flux in a rarefied gas (Problem 13.10) the shear stress too does not depend on the plate-to-plate separation and is proportional to the pressure of the gas.

In a gas that is $10^4$ times more dense, the mean free path $\langle l_f\rangle$ drops to $\sim 7.5\ \mu$m and is hence much smaller than the separation of the plates $d$. Now the intermolecular collisions are very frequent and an equilibrium velocity profile $u(z)$ is established between the plates, the velocity $u$ being a linear function of the normal coordinate $z$. Using similar arguments as in the analysis of the conduction of heat (Problem 13.10), the flux of the linear momentum at a given $z$ in the layer can be estimated by

$$\frac{\mathcal{F}}{A} = j\big[m_1 u(z + \mathrm{d}z) - m_1 u(z - \mathrm{d}z)\big]\,,$$

where $j = n\langle v\rangle/4$ and $\mathrm{d}z \approx \langle l_f\rangle$. One can write $u\big(z \pm \langle l_f\rangle\big) \approx u(z) \pm (\mathrm{d}u/\mathrm{d}z)\langle l_f\rangle$ and thus

$$\begin{aligned}\frac{\mathcal{F}}{A} &= \frac{\rho\langle l_f\rangle\langle v\rangle}{2}\frac{\mathrm{d}u}{\mathrm{d}z} \approx \frac{\rho\langle l_f\rangle\langle v\rangle u}{2d} = \frac{u}{\pi r_1^2 d}\sqrt{\frac{k_B T M}{8\pi N_A}} \\ &= 7.14\times 10^{-5}\ \mathrm{N/m^2}\,.\end{aligned}$$

Apart from the relations already used above we also inserted $\langle l_f\rangle = k_B T/4\pi r_1^2 p$ and we assumed that the molecular radius is $r_1 = 2\times 10^{-10}$ m. We note that the shear stress depends on the distance between the plates but not on pressure. In this regime we can estimate the viscosity of the gas, which reads

$$\eta = \frac{\mathcal{F}}{A}\frac{d}{u} = \frac{1}{\pi r_1^2}\sqrt{\frac{k_B T M}{8\pi N_A}} = 2.14\times 10^{-5}\ \mathrm{Ns/m^2}\,.$$

**Problem 13.14.**
*A large container is filled with vaporized silver at* 0.1 mbar *and placed into an evacuated chamber. A tiny circular hole with* 0.01 mm$^2$ *cross section is drilled in its wall. A circular plate* 1 m *in diameter is placed* 1 m *away from the hole so that their symmetry axes coincide. Calculate the force exerted on the plate by the escaping silver atoms, knowing that all atoms that hit the plate remain trapped on its surface! What is the energy flux captured by the plate? The average speed of atoms is* 240 m/s.

If gravity is neglected, the velocity of the silver atoms remains unaltered after the atoms pass through the hole. We denote the plate radius by $R$ and the hole-plate distance by $d$. All atoms with a velocity at polar angles $\theta$ smaller than $\theta_0 = \arccos\left(d/\sqrt{d^2+R^2}\right)$ (where $\theta$ is measured with respect to the symmetry axis of the hole) will eventually hit the plate and contribute to the force. By using the same notation as in Problems 13.2 and 13.3 and switching to spherical coordinates, the impulse of the force imparted by a single atom upon collision is $m_1 v\cos\theta$, whereas the impulse imparted by all atoms during a time interval $\Delta t$ reads

$$\begin{aligned}\mathcal{F}\Delta t &= nAm_1\Delta t\int_0^\infty w(v)v^4\mathrm{d}v\int_0^{\theta_0} 2\pi\cos^2\theta\sin\theta\,\mathrm{d}\theta \\ &= \frac{nAm_1\Delta t}{6}\langle v^2\rangle\left(1-\cos^3\theta_0\right).\end{aligned}$$

Now we use the equipartition theorem which states that $m_1\langle v^2\rangle/2 = 3k_B T/2$ and the ideal gas equation of state $p = nk_B T$ to find that the force is equal to

$$\mathcal{F} = \frac{pA}{2}\left(1-\cos^3\theta_0\right) = 14.2\ \mathrm{nN}.$$

If the plate approaches the hole so that $d\to 0$ and $\theta_0\to\pi/2$, the result is $\mathcal{F} = pA/2$, where the factor 1/2 is due to the fact that the atoms remain trapped on the plate rather than bounce from it.

Similarly, the kinetic energy carried by a single atom is $m_1 v^2/2$, whereas the total energy captured by the plate during a time interval $\Delta t$ is given by

$$P\Delta t = \frac{nAm_1\Delta t}{2}\int_0^\infty w(v)v^5 \mathrm{d}v \int_0^{\theta_0} 2\pi \cos\theta \sin\theta \, \mathrm{d}\theta$$

(see also Problem 13.10). Thus the energy flux is

$$P = \frac{pA}{2}\langle v\rangle \sin^2\theta_0 = 2.4 \times 10^{-6}\,\mathrm{W}.$$

**Problem 13.15.**
*A two-dimensional monatomic ideal gas effuses from a vessel through a tiny opening into vacuum. The flux of the escaping atoms is equal to* $10^{18}\,\mathrm{m^{-1}s^{-1}}$. *Calculate the number density of the gas inside the vessel if the temperature is* 300 K *and the kilomolar mass is* 4 kg/kmol*! What is the energy flux carried by the escaping atoms?*

In polar coordinates, the distribution of the velocities of atoms is given by

$$w(\mathbf{v}) = \frac{\beta m_1}{2\pi}\exp\left(-\frac{\beta m_1 v^2}{2}\right);$$

we also have $\mathrm{d}\mathbf{v} = v\mathrm{d}v\mathrm{d}\phi$, where the angle $\phi$ is measured with respect to the hole normal. We first calculate the average speed of the atoms

$$\begin{aligned}\langle v\rangle &= \int v w(\mathbf{v})\,\mathrm{d}\mathbf{v} = \frac{\beta m_1}{2\pi}\int_0^\infty \exp\left(-\frac{\beta m_1 v^2}{2}\right)v^2 \mathrm{d}v \int_0^{2\pi}\mathrm{d}\phi\\ &= \sqrt{\frac{\pi}{2\beta m_1}}.\end{aligned}$$

Here the integral over the velocities was expressed in terms of the gamma function $\Gamma(3/2) = \sqrt{\pi}/2$. The number of atoms escaping in a time interval $\Delta t$ through an opening of width $l$ is

$$\Delta N = \int nlv\cos\phi\Delta t\, w(\mathbf{v})v\,\mathrm{d}v\,\mathrm{d}\phi$$

and the corresponding flux of the atoms reads

$$j = \frac{1}{l}\frac{\Delta N}{\Delta t} = n\int_{-\pi/2}^{\pi/2}\cos\phi\,\mathrm{d}\phi\int_0^\infty v^2 w(\mathbf{v})\,\mathrm{d}v = \frac{n\langle v\rangle}{\pi}.$$

This result can be used to calculate the density of the gas $n$ which is $3.2 \times 10^{15}\,\mathrm{m}^{-2}$. In a similar manner, we can estimate the kinetic energy of atoms that pass through the hole in a time interval $\Delta t$:

$$\Delta E = \int nlv \cos\phi \Delta t \, \frac{m_1 v^2}{2} \, w(\mathbf{v}) v \, \mathrm{d}v \, \mathrm{d}\phi .$$

Thus the energy flux reads

$$\begin{aligned} j_Q &= \frac{1}{l}\frac{\Delta E}{\Delta t} = \frac{nm_1}{2}\int_{-\pi/2}^{\pi/2}\cos\phi \, \mathrm{d}\phi \int_0^\infty v^4 w(\mathbf{v}) \, \mathrm{d}v = \frac{3}{2\pi} nk_BT\langle v\rangle \\ &= \frac{3}{2}k_BTj \, . \end{aligned}$$

Here the integral over the velocities involves $\Gamma(5/2) = 3\sqrt{\pi}/4$, and the final result is $j_Q = 6.2$ mW/m. Note that like in three dimensions, a simple estimate based on the equipartition theorem gives a somewhat different result, namely $k_BTj$.

**Problem 13.16.**
*Use the statistical-mechanical description of the degenerate electron gas to calculate the electric current emitted from a tungsten electrode of a surface area of* 1 cm$^2$ *at* 2500 K*! The chemical potential and the work function of tungsten are* 9 eV *and* 4.5 eV, *respectively.*

At absolute zero, the Fermi occupation number $f(E)$ vanishes for all energy levels above the chemical potential $\mu$. At a finite temperature, however, $f(E)$ is nonzero albeit small even at energies exceeding $\mu + E_i$, where $E_i$ is the work function. In other words, some of the electrons have enough energy to escape from the metal, which is referred to as the thermionic emission. We use a coordinate system where the $z$ axis is perpendicular to the surface of the metal sample, and we denote the mass of the electron by $m$ and the components of the linear momentum of the electrons by $p_i$. The number of electrons that escape from a patch of a surface area of $A$ in a time interval $\Delta t$ reads

$$\begin{aligned} \Delta N &= 2\int \frac{Av_z\Delta t}{h^3} f(E)\mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z \\ &= \frac{2A\Delta t}{mh^3}\int_{\sqrt{2m(\mu+E_i)}}^\infty p_z\mathrm{d}p_z \int_{-\infty}^\infty \mathrm{d}p_x \int_{-\infty}^\infty \mathrm{d}p_y \, f(E) \, . \end{aligned}$$

The lower bound of the integral over the normal component of the momentum $p_z$ ensures that only electrons that are fast enough actually leave the metal. After we introduce $p'^2 = p_x^2 + p_y^2$ and note that $E = (p_z^2 + p'^2)/2m$, we find that the electron flux is given by

$$\begin{aligned} j &= \frac{4\pi}{mh^3}\int_{\sqrt{2m(\mu+E_i)}}^\infty p_z\mathrm{d}p_z \\ &\quad \times \int_0^\infty \frac{p'\mathrm{d}p'}{\exp\Big(\beta\big[(p_z^2/2m) + (p'^2/2m) - \mu\big]\Big) + 1} \\ &= \frac{4\pi k_BT}{h^3}\int_{\sqrt{2m(\mu+E_i)}}^\infty p_z\mathrm{d}p_z \ln\Big(1 + \exp\big(\beta(\mu - p_z^2/2m)\big)\Big). \end{aligned}$$

In the relevant range of $p_z$, the second term in the argument of the logarithm is much smaller than unity and thus the logarithm can be expanded to first order. The final result is

$$j = \frac{4\pi m}{h^3} k_B^2 T^2 \exp\left(-\beta E_i\right) = 4 \times 10^{22}\ \mathrm{m}^{-2}\mathrm{s}^{-1}.$$

This corresponds to an electric current of $I = j e_0 A = 0.65$ A. As shown in Problem 5.20, thermionic emission can also be analyzed on purely thermodynamic grounds, which leads to the same result—Richardson's law.

# Appendix A
# Steam Tables

The indices $l$ and $v$ refer to liquid water and vapor, respectively.

| $T$ [°C] | $p$ [bar] | $\rho_l^{-1}$ [dm$^3$/kg] | $\rho_v^{-1}$ [m$^3$/kg] | $h_l$ [kJ/kg] | $h_v$ [kJ/kg] | $\Delta h$ [kJ/kg] | $s_l$ [kJ/kg K] | $s_v$ [kJ/kg K] |
|---|---|---|---|---|---|---|---|---|
| 0 | 0.006107 | 1.0002 | 206.29 | 0 | 2500.6 | 2500.6 | 0 | 9.1545 |
| 5 | 0.008719 | 1.0001 | 147.15 | 21.0 | 2510.0 | 2489.0 | 0.0764 | 9.0242 |
| 10 | 0.01227 | 1.0004 | 106.42 | 42.0 | 2519.2 | 2477.2 | 0.1511 | 8.8996 |
| 15 | 0.01704 | 1.0010 | 77.97 | 63.0 | 2528.4 | 2465.4 | 0.2245 | 8.7803 |
| 20 | 0.02337 | 1.0018 | 57.84 | 83.9 | 2537.6 | 2453.7 | 0.2964 | 8.6662 |
| 25 | 0.03166 | 1.0030 | 43.40 | 104.8 | 2546.7 | 2441.9 | 0.3671 | 8.5569 |
| 30 | 0.04242 | 1.0044 | 32.93 | 125.7 | 2555.7 | 2430.0 | 0.4366 | 8.4523 |
| 35 | 0.05622 | 1.0061 | 25.25 | 146.6 | 2564.7 | 2418.1 | 0.5050 | 8.3520 |
| 40 | 0.07375 | 1.0079 | 19.55 | 167.5 | 2573.7 | 2406.2 | 0.5722 | 8.2559 |
| 45 | 0.09582 | 1.0099 | 15.28 | 188.4 | 2582.6 | 2394.2 | 0.6384 | 8.1637 |
| 50 | 0.12335 | 1.0121 | 12.045 | 209.3 | 2591.5 | 2382.2 | 0.7036 | 8.0752 |
| 55 | 0.1574 | 1.0145 | 9.578 | 230.2 | 2600.3 | 2370.1 | 0.7678 | 7.9902 |
| 60 | 0.1992 | 1.0171 | 7.678 | 251.1 | 2609.0 | 2357.9 | 0.8311 | 7.9085 |
| 65 | 0.2501 | 1.0199 | 6.201 | 272.1 | 2617.7 | 2345.6 | 0.8934 | 7.8299 |
| 70 | 0.3116 | 1.0228 | 5.045 | 293.0 | 2626.3 | 2333.3 | 0.9549 | 7.7543 |
| 75 | 0.3855 | 1.0258 | 4.133 | 314.0 | 2634.8 | 2320.8 | 1.0155 | 7.6815 |
| 80 | 0.4736 | 1.029 | 3.408 | 335.0 | 2643.2 | 2308.2 | 1.0753 | 7.6114 |
| 85 | 0.5780 | 1.032 | 2.828 | 356.0 | 2651.6 | 2295.6 | 1.1344 | 7.5438 |
| 90 | 0.7011 | 1.036 | 2.361 | 377.0 | 2659.8 | 2282.8 | 1.1926 | 7.4785 |
| 95 | 0.8453 | 1.040 | 1.982 | 398.0 | 2667.9 | 2269.9 | 1.2501 | 7.4155 |
| 100 | 1.0133 | 1.043 | 1.673 | 419.1 | 2675.8 | 2256.7 | 1.3070 | 7.3546 |
| 105 | 1.208 | 1.047 | 1.419 | 440.2 | 2683.7 | 2243.5 | 1.3631 | 7.2957 |
| 110 | 1.433 | 1.052 | 1.210 | 461.4 | 2691.4 | 2230.0 | 1.4186 | 7.2387 |
| 115 | 1.691 | 1.056 | 1.036 | 482.5 | 2698.9 | 2216.4 | 1.4734 | 7.1834 |
| 120 | 1.985 | 1.060 | 0.8917 | 503.8 | 2706.3 | 2202.5 | 1.5277 | 7.1298 |
| 125 | 2.321 | 1.065 | 0.7704 | 525.0 | 2713.5 | 2188.5 | 1.5814 | 7.0779 |
| 130 | 2.701 | 1.070 | 0.6684 | 546.4 | 2720.5 | 2174.1 | 1.6345 | 7.0273 |

(continued)

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| $T$[°C] | $p$ [bar] | $\rho_l^{-1}$ [dm$^3$/kg] | $\rho_v^{-1}$ [m$^3$/kg] | $h_l$ [kJ/kg] | $h_v$ [kJ/kg] | $\Delta h$ [kJ/kg] | $s_l$ [kJ/kg K] | $s_v$ [kJ/kg K] |
|---|---|---|---|---|---|---|---|---|
| 135 | 3.131 | 1.075 | 0.5820 | 567.7 | 2727.4 | 2159.7 | 1.6870 | 6.9782 |
| 140 | 3.614 | 1.080 | 0.5087 | 589.2 | 2734.0 | 2144.8 | 1.7391 | 6.9304 |
| 145 | 4.155 | 1.085 | 0.4461 | 610.6 | 2740.4 | 2129.8 | 1.7906 | 6.8838 |
| 150 | 4.760 | 1.091 | 0.3926 | 632.2 | 2746.6 | 2114.4 | 1.8417 | 6.8384 |
| 155 | 5.433 | 1.096 | 0.3465 | 653.8 | 2752.5 | 2098.7 | 1.8923 | 6.7940 |
| 160 | 6.180 | 1.102 | 0.3069 | 675.5 | 2758.2 | 2082.7 | 1.9425 | 6.7506 |
| 165 | 7.008 | 1.108 | 0.2725 | 697.3 | 2763.6 | 2066.3 | 1.9923 | 6.7082 |
| 170 | 7.920 | 1.114 | 0.2426 | 719.2 | 2768.7 | 2049.5 | 2.0417 | 6.6666 |
| 175 | 8.925 | 1.121 | 0.2166 | 741.1 | 2773.6 | 2032.5 | 2.0907 | 6.6258 |
| 180 | 10.027 | 1.128 | 0.1939 | 763.2 | 2778.1 | 2014.9 | 2.1394 | 6.5858 |
| 185 | 11.23 | 1.134 | 0.1739 | 785.3 | 2782.3 | 1997.0 | 2.1877 | 6.5464 |
| 190 | 12.55 | 1.142 | 0.1564 | 807.6 | 2786.2 | 1978.6 | 2.2356 | 6.5077 |
| 195 | 13.99 | 1.149 | 0.1409 | 829.9 | 2789.7 | 1959.8 | 2.2833 | 6.4695 |
| 200 | 15.55 | 1.157 | 0.1272 | 852.4 | 2792.9 | 1940.5 | 2.3307 | 6.4318 |
| 205 | 17.25 | 1.164 | 0.1151 | 875.0 | 2795.6 | 1920.6 | 2.3779 | 6.3945 |
| 210 | 19.08 | 1.173 | 0.10427 | 897.8 | 2798.0 | 1900.2 | 2.4247 | 6.3576 |
| 215 | 21.06 | 1.181 | 0.09465 | 920.7 | 2799.9 | 1879.2 | 2.4714 | 6.3211 |
| 220 | 23.20 | 1.190 | 0.08606 | 943.7 | 2801.5 | 1857.8 | 2.5179 | 6.2849 |
| 225 | 25.50 | 1.199 | 0.07837 | 966.9 | 2802.6 | 1835.7 | 2.5641 | 6.2490 |
| 230 | 27.98 | 1.209 | 0.07147 | 990.3 | 2803.3 | 1813.0 | 2.6103 | 6.2133 |
| 235 | 30.64 | 1.219 | 0.06527 | 1013.9 | 2803.4 | 1789.5 | 2.6562 | 6.1778 |
| 240 | 33.48 | 1.229 | 0.05967 | 1037.7 | 2803.1 | 1765.4 | 2.7021 | 6.1425 |
| 245 | 36.53 | 1.240 | 0.05463 | 1061.6 | 2802.3 | 1740.7 | 2.7479 | 6.1072 |
| 250 | 39.78 | 1.251 | 0.05006 | 1085.8 | 2800.9 | 1715.1 | 2.7936 | 6.0719 |
| 255 | 43.24 | 1.263 | 0.04592 | 1110.3 | 2799.0 | 1688.7 | 2.8392 | 6.0366 |
| 260 | 46.94 | 1.276 | 0.04215 | 1135.0 | 2796.5 | 1661.5 | 2.8849 | 6.0012 |
| 265 | 50.87 | 1.289 | 0.03872 | 1160.0 | 2793.3 | 1633.3 | 2.9306 | 5.9657 |
| 270 | 55.05 | 1.302 | 0.03560 | 1185.3 | 2789.5 | 1604.2 | 2.9764 | 5.9299 |
| 275 | 59.49 | 1.317 | 0.03275 | 1210.9 | 2784.9 | 1574.0 | 3.0223 | 5.8938 |
| 280 | 64.19 | 1.332 | 0.03013 | 1236.8 | 2779.6 | 1542.8 | 3.0683 | 5.8573 |
| 285 | 69.18 | 1.348 | 0.02774 | 1263.2 | 2773.4 | 1510.2 | 3.1145 | 5.8203 |
| 290 | 74.45 | 1.366 | 0.02554 | 1289.9 | 2766.4 | 1476.5 | 3.1610 | 5.7827 |
| 295 | 80.03 | 1.384 | 0.02351 | 1317.2 | 2758.4 | 1441.2 | 3.2078 | 5.7444 |
| 300 | 85.92 | 1.404 | 0.02164 | 1344.9 | 2749.3 | 1404.4 | 3.2549 | 5.7051 |
| 305 | 92.14 | 1.425 | 0.01992 | 1373.2 | 2739.0 | 1365.8 | 3.3026 | 5.6648 |
| 310 | 98.70 | 1.448 | 0.01832 | 1402.1 | 2727.3 | 1325.2 | 3.3508 | 5.6232 |
| 315 | 105.61 | 1.472 | 0.01683 | 1431.8 | 2714.2 | 1282.4 | 3.3996 | 5.5800 |
| 320 | 112.90 | 1.499 | 0.01545 | 1462.2 | 2699.7 | 1237.5 | 3.4493 | 5.5356 |
| 325 | 120.57 | 1.529 | 0.01417 | 1493.6 | 2683.6 | 1190.0 | 3.5001 | 5.4895 |
| 330 | 128.64 | 1.562 | 0.01297 | 1526.0 | 2665.5 | 1139.5 | 3.5520 | 5.4412 |
| 335 | 137.14 | 1.599 | 0.01184 | 1559.7 | 2645.2 | 1085.5 | 3.6054 | 5.3903 |
| 340 | 146.08 | 1.639 | 0.01078 | 1594.9 | 2622.1 | 1027.2 | 3.6606 | 5.3359 |
| 345 | 155.48 | 1.686 | 0.00977 | 1631.9 | 2595.4 | 963.5 | 3.7181 | 5.2769 |
| 350 | 165.37 | 1.741 | 0.00881 | 1671.2 | 2564.3 | 893.1 | 3.7788 | 5.2119 |
| 355 | 175.77 | 1.807 | 0.00787 | 1713.9 | 2527.0 | 813.1 | 3.8441 | 5.1386 |
| 360 | 186.74 | 1.894 | 0.00694 | 1761.5 | 2481.1 | 719.6 | 3.9164 | 5.0529 |
| 365 | 198.29 | 2.016 | 0.00599 | 1817.6 | 2420.9 | 603.3 | 4.0010 | 4.9465 |
| 370 | 210.52 | 2.225 | 0.00493 | 1892.4 | 2330.8 | 438.4 | 4.1137 | 4.7953 |
| 374.15 | 221.29 | 3.1 | 0.0031 | 2084.0 | 2084.0 | 0 | 4.4062 | 4.4062 |

# Appendix B
# Metropolis Algorithm

In virtually all problems of statistical physics, one must evaluate the partition function of the system considered. As seen in the previous chapters, this can be done exactly in some cases; in others, one has to resort to suitable approximations. Unfortunately, such an approximation does not exist in all cases or may be inconsistent or untractable so that an entirely different approach is required. It is easy to see that a direct numerical evaluation of the canonical partition function

$$\exp(-\beta F) \propto \int_\Gamma \exp\big(-\beta E(\mathbf{u})\big)\,\mathrm{d}\mathbf{u}$$

where the vector $\mathbf{u}$ denotes a multi-particle state in the phase space, is not a viable option. The phase space $\Gamma$ is simply too large for such an integration to be feasible, and by carrying it out, most of the computing time would be spent in the regions of the phase space where the statistical weight $\exp\big(-\beta E(\mathbf{u})\big)$ is negligibly small.

However, there is a way around this problem. Usually one is not interested in the partition function as such but rather in an equilibrium average of a given quantity

$$\langle A\rangle = \frac{\int_\Gamma A(\mathbf{u})\exp\big(-\beta E(\mathbf{u})\big)\,\mathrm{d}\mathbf{u}}{\int_\Gamma \exp\big(-\beta E(\mathbf{u})\big)\,\mathrm{d}\mathbf{u}}$$

which actually corresponds to a ratio of two non-computable integrals. In other words: When computing averages, it is sufficient to know the relative probabilities of occurrence within a limited set of selected states $\mathbf{u}$. When selecting these states, it is advisable to cover those regions of the phase space where the statistical weight is onnegligible. By increasing the number of selected states, the estimate of the average $\langle A\rangle$ is improved. These ideas are the basis of the so-called Metropolis algorithm sketched below.

Suppose that one can generate a representative set of $L$ sample points $\mathbf{u}$ in the phase space in such a way that their density is proportional to the probability density $\rho(\mathbf{u}) \propto \exp\big(-\beta E(\mathbf{u})\big)$. Then $\langle A\rangle$ is obtained by simply averaging the quantity $A$ over the selected $L$ points. There is no need that all of these points be generated at

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once; instead, one can invent a suitable trajectory through phase space that visits the points one after another.

We start building the trajectory at a point $\mathbf{u}'$ called "old" ($o$) and randomly select another point $\mathbf{u}$ called "new" ($n$). The $o \to n$ move can be a translation and/or rotation of a molecule (or a molecular cluster), a spin-flip, particle insertion/removal, etc. The probability that the move $o \to n$ be executed $\pi(o \to n)$ is a product of the probability that the move be proposed $\alpha(o \to n)$ and the probability that the move be accepted $\sigma(o \to n)$. This scheme of generating new points has to be ergodic: It must ensure that all parts of the phase space are reachable within a finite number of steps. In equilibrium, the statistical weights $\rho(o)$ and $\rho(n)$ of states $o$ and $n$ differ. For $\rho(n) > \rho(o)$ (i.e., the new state is more probable than the old one), the $o \to n$ move is accepted unconditionally; otherwise, this is done with a probability $P < 1$. Its value is determined by requiring that, in an already equilibrated system, further transitions between states must not ruin the existing equilibrium: The numbers of implemented transitions $o \to n$ and $n \to o$ must be the same. This can be formulated in terms of the so-called detailed balance condition: $\rho(o)\pi(o \to n) = \rho(n)\pi(n \to o)$. By assuming that $\alpha(o \to n) = \alpha(n \to o)$, we can recast this condition in case of the canonical distribution as

$$\frac{\sigma(o \to n)}{\sigma(n \to o)} = \frac{\rho(n)}{\rho(o)} = \exp\big(-\beta[E(n) - E(o)]\big).$$

From here, it immediately follows that

$$P = \exp\big(-\beta[E(n) - E(o)]\big).$$

After a proposed new state is either accepted and relabeled "old" or rejected, the entire procedure is repeated, thereby gradually building the entire trajectory. The density of the thus generated points of the phase space $L$ is proportional to $\exp\big(-\beta E(\mathbf{u})\big)$.

In each step, the quantity of interest $A$ has to be computed and added to the average. This has to be done even if the $o \to n$ move has been rejected. In cases where the trajectory starts from a nonequilibrium state, the accumulation of averages must be postponed until the system reaches equilibrium. The approach to equilibrium can be monitored by plotting the behavior of the energy or another suitable variable. The fraction of the rejected moves can be controlled by dynamically adjusting the amplitude of the trial moves $o \to n$; an efficient sampling of the phase space typically requires a move acceptance ratio of around one half. Such an evaluation of thermodynamic averages is called a Monte Carlo simulation.

The above algorithm can be applied for average calculations even if the $\rho(\mathbf{u})$ distribution is not canonical—a generalization of the above acceptance criterion to other distributions is straightforward. In the isothermal–isobaric ensemble, for example, the distribution derived in Problem 8.5 should be used.

The above Metropolis algorithm can also serve as a rather general and robust tool for the numerical minimization of functions. If we employ, e.g., the canonical distribution as the probability density, the minimized quantity is the energy of the system. The moves that increase the energy ensure that the minimization trajectory does not get stuck in the local minima. By gradually cooling the system, we eventually find the global energy minimum. This approach is known as simulated annealing.

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